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THE CONTRIBUTION OF BOUND, METASTABLE, AND FREE MOLECULES TO THE SECOND VIRIAL COEFFICIENT [*]

(REVISED)

by

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ABSTRACT

The second virial coefficient for molecules interacting with a spherically symmetric potential is divided into three parts: (1) a contribution B_b, related to the equilibrium constant for the formation of bound double molecules; (2) a contribution B_m, related to the equilibrium constant for the formation of metastably bound double molecules; and (3) a contribution B_f, due to molecules which interact but are free to separate after the interaction. Equations are given for determining each of the three parts of the second virial coefficients. A detailed treatment of these three contributions is presented for the square well, Sutherland, and Lennard-Jones ~~(6-12)~~ potentials.

The mean lifetimes of metastably bound double molecules are discussed and it is found that most metastably bound double molecules have mean lifetimes considerably longer than the mean time between collisions at ordinary pressures. Finally, an equation is developed for the number of vibrational levels of a double molecule.

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THE CONTRIBUTION OF BOUND, METASTABLE, AND FREE MOLECULES TO THE SECOND VIRIAL COEFFICIENT AND SOME PROPERTIES OF DOUBLE MOLECULES

I. INTRODUCTION:

The equation of state of a dilute gas can be expanded in the virial form

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \ldots \tag{1}$$

Here, $B(T)$, the second virial coefficient can be expressed in terms of the energy of interaction between pairs of molecules. If the intermolecular potential, $\phi(r)$, depends only on the separation, r, and not on the relative orientations of the two molecules, then

$$B(T) = 2\pi N \int_0^\infty \left[1 - e^{-\phi(r)/kT} \right] r^2 \, dr \tag{2}$$

This relationship is easy to derive from statistical mechanical arguments and has been used[1] since 1908 and maybe earlier. The simplicity of the second virial coefficient in terms of the intermolecular potential arises from the fact that the equation of state is an equilibrium property.

The second virial coefficient can be broken up into three parts,

$$B(T) = B_f(T) + B_b(T) + B_m(T) \tag{3}$$

Here $B_f(T)$ arises from collisions between free molecules; $B_b(T)$ is related to the equilibrium constant for the formation of bound double molecules (or dimers) in the gas; and $B_m(T)$ is related to the equilibrium constant for the formation of metastable double molecules (or

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[1] L. S. Ornstein, Thesis, Leiden 1908.

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dimers) which, according to quantum mechanics, can dissociate but which, according to classical mechanics, are firmly bound. Terrell Hill[2] has derived the equation for $Q_b(T)$, the partition function for bound double molecules, and from this we obtain $B_b(T)$. In the present paper, we also derive the relations between $B_m(T)$, $B_f(T)$, and the intermolecular potential. Since $B_b(T)$ and $B_m(T)$ are related to the equilibrium constants for dimerization, a knowledge of these quantities is useful in developing a theory for the variations of the transport coefficients with pressure due to the formation of dimers. The dissociation of metastable molecules and its effects on the transport properties of a gas will be discussed later. It will be seen that the dissociation of metastable molecules leads to a small quantum correction for the transport coefficients at low temperatures.

Whenever the potential is purely repulsive, so that no bound or metastable dimers exist, the second virial coefficient can be expressed in terms of a collision integral which involves the angles of deflection of the binary collision trajectories. Detailed equations are given for determining $B_f(T)$, $B_b(T)$, and $B_m(T)$ for an arbitrary intermolecular potential. For molecules satisfying the square well, Sutherland (attractive term proportional to r^{-6}), or Lennard-Jones (6-12) potential, tables of values and graphs are given for $B_f^* = B_f/b_o$, $B_b^* = B_b/b_o$, and $B_m^* = B_m/b_o$ as functions of the reduced temperature $T^* = kT/\epsilon$. Here, $b_o = (2/3) \pi N \sigma^3$. The novelty of our treatment consists in distinguishing between the bound and the metastably bound double molecules. The introduction of the two types of double molecules

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[2] T. L. Hill, J. Chem. Phys. 23, 617, (1955); "Statistical Mechanics", (McGraw-Hill, 1956), Ch. 5.

is necessary to remove the ambiguities in the various definitions of double molecules. Some authorities, such as Terrell Hill[2], have not considered the existence or effect of the metastable species.

Non-equilibrium properties of gases such as the transport coefficients are much more complicated functions of the intermolecular potential than are the second virial coefficients. For example, the transport coefficients in the limit of low pressure can be expressed[3] in terms of the collision integrals

$$\Omega^{(l,s)}(T) = \pi^{1/2}\left(\frac{\mu}{2kT}\right)^{s+1/2} \int_0^\infty e^{-\mu g^2/2kT} g^{2s+3} \int_0^\infty (1-\cos^l \chi)\, b\, db\, dg \qquad (4)$$

Here μ is the reduced mass of the colliding molecules, $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$; g is the initial relative velocity of the two molecules; b is the impact parameter or the distance of closest approach of the two molecules if their relative trajectory persists in a straight line; and $\chi(b, g)$ is the angle of deflection of the relative trajectories which results from the intermolecular potential (see Fig. 1). The angle of deflection can be expressed in terms of the intermolecular potential,

$$\chi(b,g) = \pi - 2b \int_{r_m}^\infty \frac{dr}{r^2 \sqrt{1 - \frac{2\phi(r)}{\mu g^2} - \frac{b^2}{r^2}}} \qquad (5)$$

Here r_m is the distance of closest approach in the actual collision, or r_m is the largest value of r for which

$$1 - \frac{2\phi(r)}{\mu g^2} - \frac{b^2}{r^2} = 0 \qquad (6)$$

If $\phi(r)$ corresponds to a purely repulsive potential, as shown in Fig. 1a, then $\chi(b, g)$ is always positive; if $\phi(r)$ is a purely attractive

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[3] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", (John Wiley, 1954), p. 484.
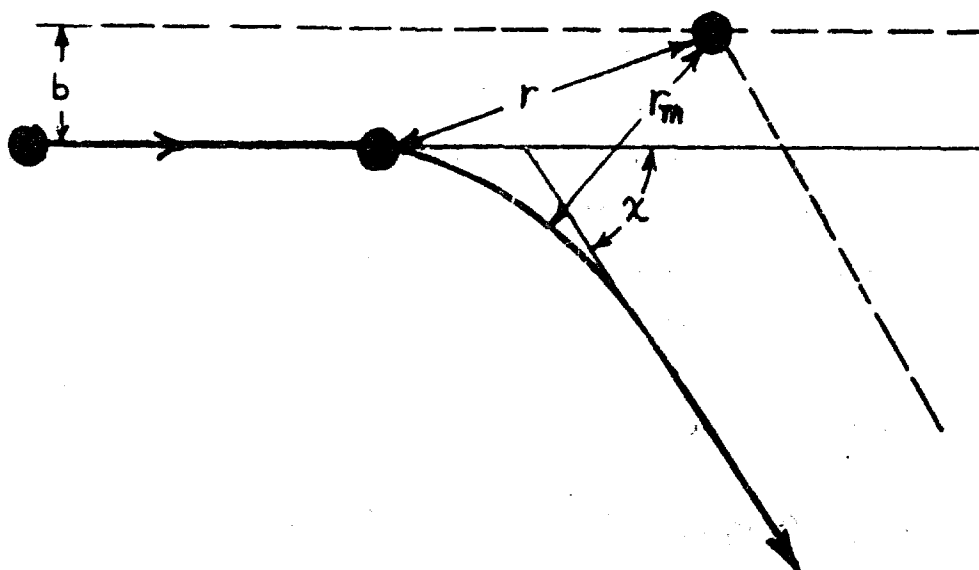
Fig. 1a. Trajectory of Collision with Repulsive Potential. Here χ is positive.
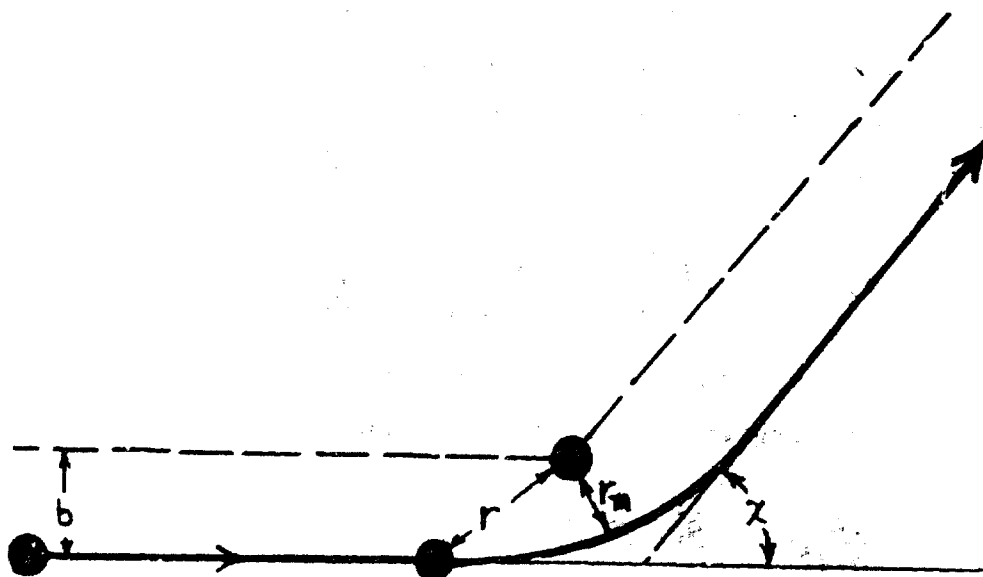

Fig. 1b. Trajectory of Collision with Attractive Potential. Here χ is negative.

potential, as shown in Fig. 1 b, then $\chi(b, g)$ is always negative; and if $\phi(r)$ corresponds to attraction for large separations and repulsion for small separations (as is usually the case), $\chi(b, g)$ is positive for some values of the parameters and negative for others.

It is convenient to define the effective potential energy as

$$\phi_{eff}(r, L) = \phi(r) + L/r^2 \tag{7}$$

Here $L = Kb^2$ where K is the initial relative kinetic energy or the total energy in the center of mass coordinate system, $K = \mu g^2/2$. Insofar as the separation between molecules as a function of time is concerned, the kinematics are the same as for the one dimensional motion of a particle of mass μ and energy K moving in the potential field $\phi_{eff}(r, L)$. The term L/r^2 is known as the centrifugal potential. The angular momentum of the collision system is $M = \mu g b$ and the moment of inertia of the collision system is $I = \mu r^2$. Thus the centrifugal potential $L/r^2 = M^2/2I$, which is the usual form for the energy of rotational motion. Fig. 2 shows a set of effective potential energy curves for the Lennard-Jones (6 12) potential,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{8}$$

Here $(-\epsilon)$ is the maximum energy of attraction between two molecules and σ is the low velocity collision diameter. It is seen from Fig. 2 that ϕ_{eff} has an inflection point at $.8\epsilon$ when $L = L_c = 2.4624\epsilon \sigma^2$. The value of ϕ_{eff} at its inflection point is known as the critical energy, K_c. The value of K_c depends upon the functional form of the intermolecular potential. The critical value of b is defined as $b_c = (L_c/K_c)^{\frac{1}{2}}$. Thus for the Lennard-Jones (6-12) potential, $b_c = (3/5^{1/3})\sigma = 1.75441\sigma$. For values of L greater than L_c, the effective potential curves have no minima and vary

Fig. 2. Effective Potential Energy Curves for the Lennard-Jones (6-12) Potential for Several Values of the Angular momentum M. Here, $L = M^2/2\mu$.
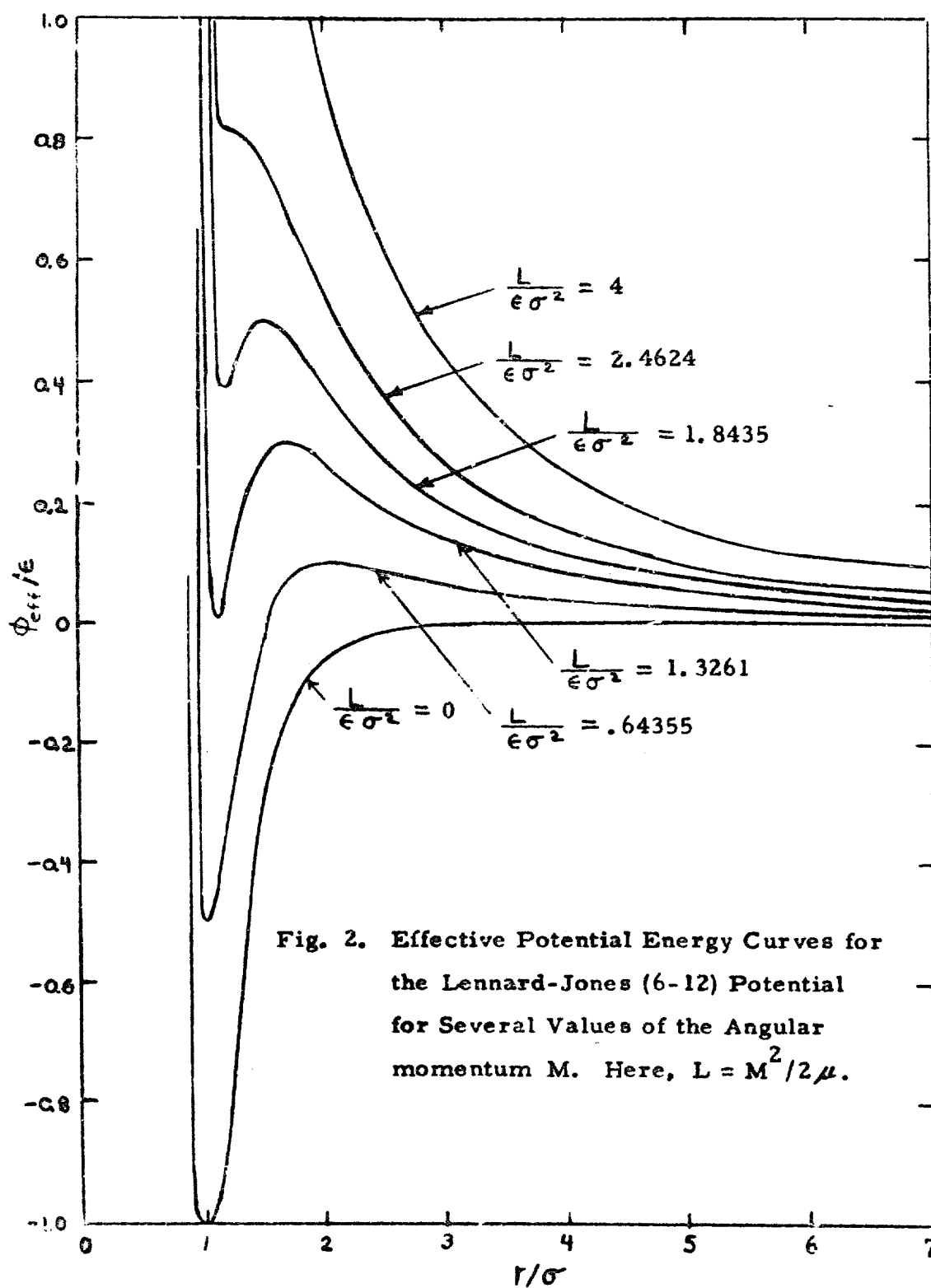
monotonically with the separation. For values of L smaller than L_c, the effective potentials have both a minimum and a maximum. The energy of the maximum varies between zero and 0.8ϵ ; and the energy of the minimum varies betweeen $(-\epsilon)$ and 0.8ϵ . Maxima in ϕ_{eff} occur when the intermolecular potential is attractive at long ranges and the attractive term varies inversely with a power of the separation greater than two.

In Fig. 3, there are two cross-hatched areas, one labeled "B" and the other "M". The region "B" corresponds to those two mole-cule systems where the total energy is less than the energy of the separated molecules. The systems in "B" correspond to bound molecules where the molecules can only be freed by a collision with another molecule. However, the "M" systems have energy greater than that of the separated molecules. From the point of view of classical mechanics, these molecules can only be freed by a collision with another molecule, but from the standpoint of quantum mechanics, the "M" systems are metastable double molecules which can dis-sociate by leakage through the energy barrier. If the half-life for dissociation is greater than the average time between collisions, the "M" systems behave like bound double molecules. But, if the time between collisions is long compared to the half-life for dissociation, the "M" systems behave more like free molecules. The mean life-times of metastable molecules will be discussed in section V. For example, in the case of argon molecules, it is found that the mean lifetime may vary between about 10^{-11} sec. to well over 10^{10} sec. depending on the particular value of the relative energy and angular momentum of the metastable pair.

Now consider one of the effective potential curves for a small value of L, as shown in Fig. 3. This effective potential has a maximum value $F(L)$. Since F is a monotonically varying function
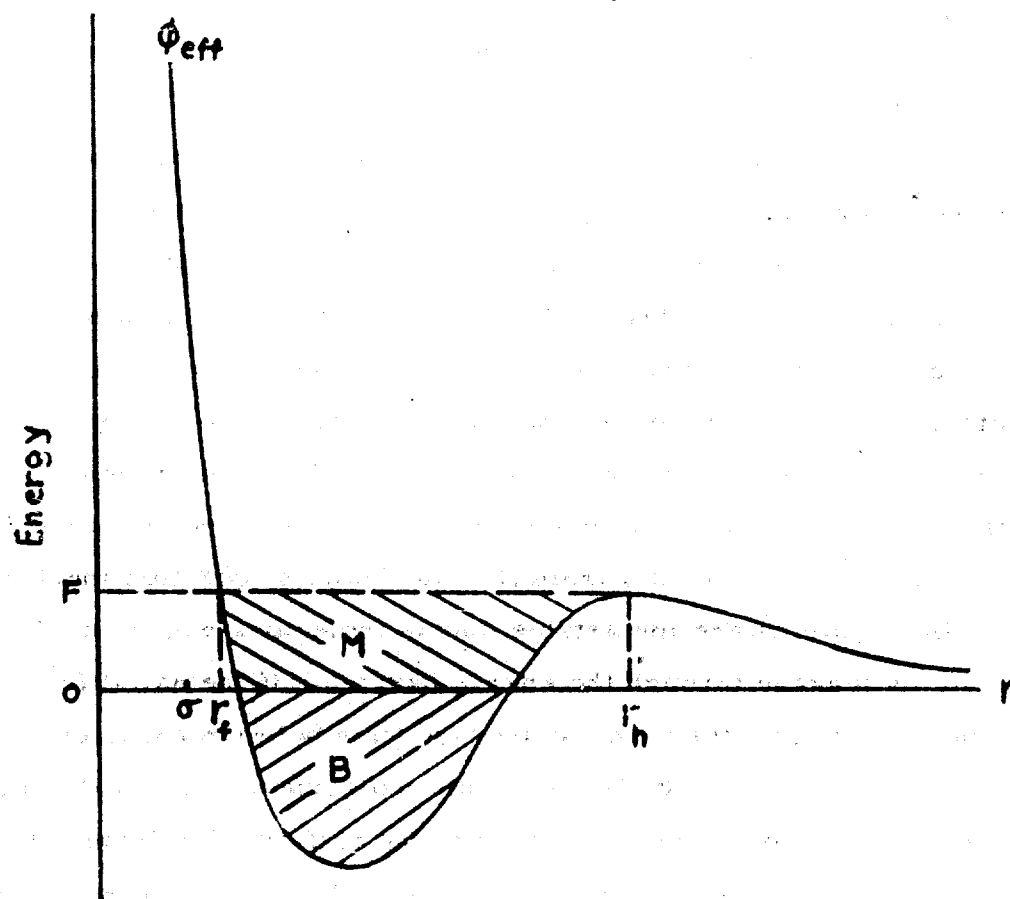
Fig. 3. Typical Effective Potential Energy Curve for a Small
Value of the Angular Momentum or a Small Value of
$L = Kb^2$.

of L, we can invert this relation to obtain L as a function of F.
Thus the family of effective potential curves with F less than or equal
to K_c can be characterized by their value of F rather than by their
value of L. As is shown in Fig. 3, the intermolecular separation at
the hump or maximum in the effective potential is $r_h(F)$. Also,
$r_f(F)$ is the smaller separation for which the effective potential has
the value F. In the limit that F approaches zero, r_h approaches
infinity and r_f approaches σ . In the other limit that F approaches
K_c, r_h becomes equal to r_f. The distance of closest approach, r_m,
of two colliding molecules can be characterized by K and F. Con-
siderable interest is attached to those collisions in which K is very
nearly equal to F. In such collisions, the two molecules orbit around
each other a number of times before they finally separate[4]. If K is
just slightly smaller than τ then r_m is slightly larger than r_h;
whereas if K is just slightly larger than F, then r_m is slightly
smaller than r_f. Since small kinetic energy, $K \leq K_c$, is required
for orbiting, it follows that such collisions are only frequent at low
temperatures.

There is still another way that we can characterize the effective
potential energy curves which have humps. Let us define $b_f(F)$ as
the value of b for which the initial kinetic energy K is equal to F.
Since $L(F) = Kb^2$, it follows that

$$b_f(F) = [L(F)/F]^{1/2}$$

Here b_f varies monotonically with F from the value infinity when
$F = 0$ to b_c when $F = K_c$. Thus b_f might be used to characterize
the effective potential curves with low values of the angular

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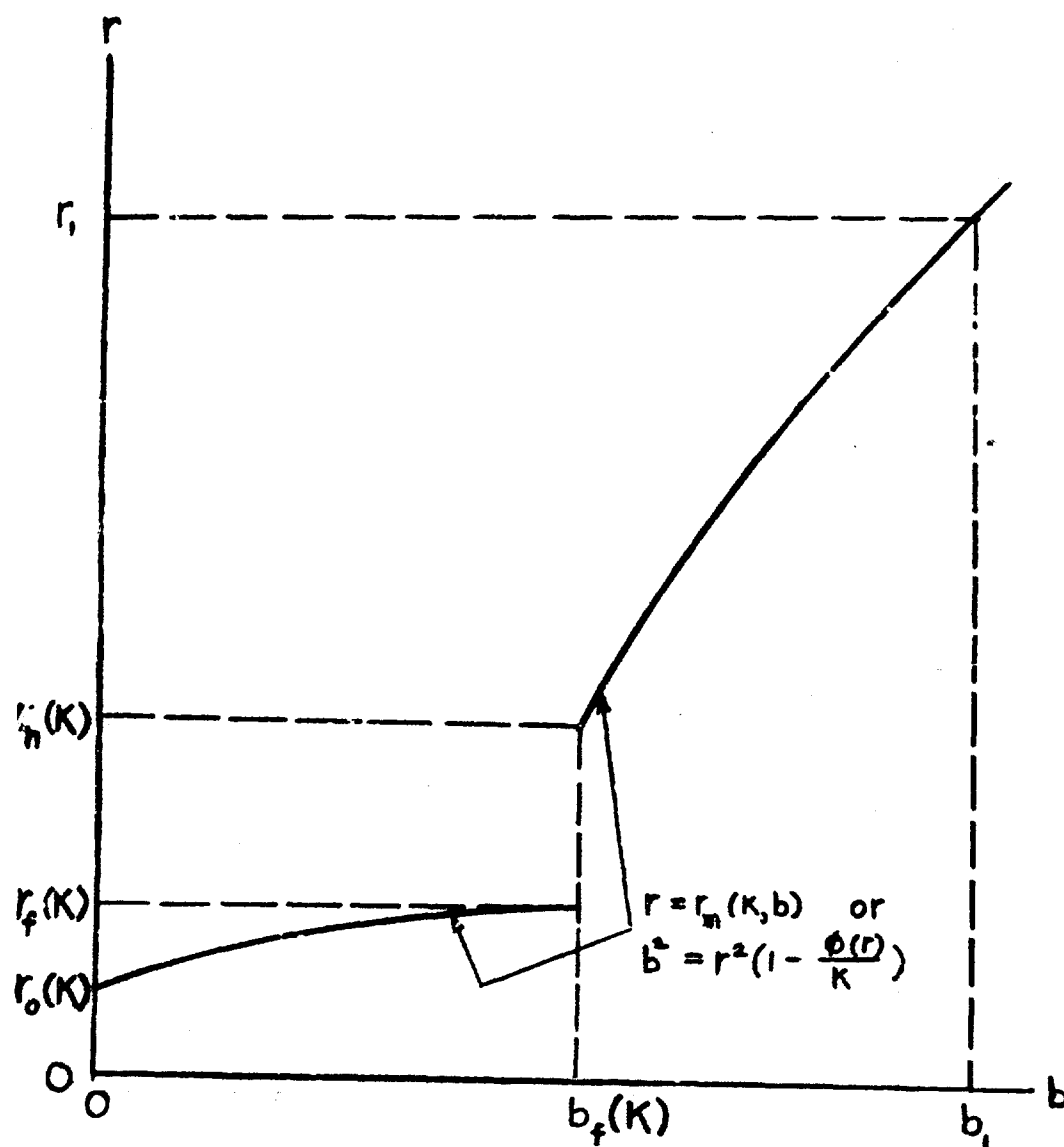[4] See Reference 3, M. T. G. L., pages 45 and 553.

Fig. 4. The distance of closest approach r_m as a function of b for a fixed value of the initial kinetic energy K less than K_c.

momentum. The significance of b_f is shown in Fig. 4. Here, for a particular value of K (less than K_c) the values of r_m are plotted as a function of b. From Eq. (6) it follows that

$$b^2 = r_m^2 \left[1 - \frac{\phi(r_m)}{K} \right] \tag{9}$$

When $b = b_f(K)$ there is a discontinuity in r_m. When b is just slightly greater than $b_f(K)$, the energy of the system is not great enough to get over the potential hump and r_m is slightly greater than $r_h(K)$. Whereas, when b is slightly less than $b_f(K)$, then r_m is slightly less than $r_f(K)$. When b is zero, r_m becomes equal to $r_o(K)$ which is defined in terms of the equation,

$$\phi(r_o) = K$$

The meaning of r_1 and b_1 will be explained in a later section. However, since $\phi(r_m)$ becomes small as r_m becomes large, it follows from Eq. (9) that the value of b approaches the value of r_m as r_m becomes large for a fixed value of K.

The second virial coefficient, $B(T)$, for spherically symmetric molecules can be written as

$$B(T) = -N\Lambda^6 Q_2/V + N\Lambda^6 Q_1^2/2V \tag{10}$$

where Q_1 and Q_2 are partition functions for one and two particles respectively, N is Avogadro's number, V is the volume, and $\Lambda^2 = h^2/2\pi m k T$. The partition function Q_1 involves integrations over the volume in which the particle is contained and over the momenta of the center of mass of the particle. The two particle partition function, Q_2, involves an integration over the volume in which the two particle system is contained, an integration over the relative coordinates of the two particles, an integration over the momenta

of the center of mass, and an integration over the relative momenta of the two particles.

Systems "B" and "M" of Fig. 3 have partition functions Q_{2b} and Q_{2m} respectively. They involve integrations over the same variables as Q_2. However, the integration limits are restricted so that the two molecules remain in the regions "B" and "M" indicated in Fig. 3. The integration limits are discussed in more detail in section III. Then, $B_b(T)$ and $B_m(T)$ are defined by the equations

$$B_b(T) = -N\Lambda^6 Q_{2b}/V \tag{11}$$

$$B_m(T) = -N\Lambda^6 Q_{2m}/V \tag{12}$$

The partition function of all other possible systems in Fig. 3 is Q_{2f}. Again, Q_{2f} contains integrations over the same variables as Q_2, but the integration limits are such that the two molecules remain outside of the regions "B" and "M". One sees that these systems correspond to molecules which interact but are free to separate to infinite distances after the interaction. The definition of $B_f(T)$ is

$$B_f(T) = -N\Lambda^6 Q_{2f}/V + N\Lambda^6 Q_1^2/2V \tag{13}$$

The role of double molecules in the second virial coefficient has long been recognized. We will now show that the equilibrium constant

$$K(T) = n_2 z_2 V/n_1^2 z_1^2 \tag{14}$$

is given by

$$-K(T) = B_f(T) + B_m(T) \tag{15}$$

In Eq. (14), n_1 and n_2 are the number of moles of single and double molecules (i.e. $n_2 = n_{2b} + n_{2m}$; the subscripts b and m refer to bound and metastable double molecules respectively) and γ_1 and γ_2 are activity coefficients. At low pressures, the activity coefficients approach unity. From the equations given in Hill's paper[5], one easily obtains the relation

$$n_2 V/n_1^2 = \Lambda^6 (Q_{2b} + Q_{2m}) N/V + a n + \ldots \tag{16}$$

The right side of this equation is a power series in n which is defined by

$$n = n_1 + 2 n_2 + 3 n_3 + \ldots$$

The number of moles of "triple molecules" is n_3, etc. The coefficient "a" involves integrals over certain regions of the phase space of one, two, and three molecules respectively. Higher coefficients depend on integrals over part of the phase space of greater numbers of molecules. Comparison of Eq. (16) with Eqs. (11) and (12) shows

$$n_2 V/n_1^2 = - (B_b + B_m) + a n + \ldots \tag{17}$$

The equilibrium constant, $K(T)$, is equal to $n_2 V/n_1^2$ in the limit that n approaches zero because under this condition the activity coefficients approach unity. Thus, Eq. (15) for $K(T)$ follows from Eqs. (14) and (17).

The equilibrium constant, $K(T)$, can be written as

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[5] Reference 2.

$$\chi(T) = \chi_b(T) + \chi_m(T) \tag{18}$$

where $\chi_b(T)$ is the equilibrium constant for bound double molecules and $\chi_m(T)$ is the equilibrium constant for metastable double molecules. It follows, for reasons similar to those given for $\chi(T)$, that $-\chi_b(T) = B_b(T)$ and $-\chi_m(T) = B_m(T)$.

In section III it will be seen that $B_b(T)$ and $B_m(T)$ must be negative so that the equilibrium constants are positive as they should be. This is to be contrasted with the results of previous attempts to relate the second virial coefficient to the equilibrium constant for dimer formation. In these previous attempts, because of the approximations made, either a negative equilibrium constant[6] is obtained at moderate and high temperatures or the introduction of an excluded volume due to the finite size of molecules obviates the necessity of dealing with a negative equilibrium constant[7,8,9]. The equations derived in section III will relate the equilibrium constant to the intermolecular potential without the introduction of any empirical concepts.

The effects of interactions between two free molecules is represented by $B_f(T)$; Eq. (55) shows how $B_f(T)$ depends on the angle of deflection due to a collision. If it is desired, $B_f(T)$ can be related to the empirical concept of excluded volume by supposing that a gas is

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[6] H. W. Woolley, J. Chem. Phys. _21_, 236 (1953).

[7] J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, J. Chem. Phys. _10_, 201 (1942).

[8] W. Weltner, Jr., J. Chem. Phys. _22_, 153 (1954).

[9] R. Ginell, J. Chem. Phys. _23_, 2395 (1955).

composed of n_1 moles of single molecules and n_2 moles of double molecules satisfying the equation of state

$$P(V - b') = (n_1 + n_2)RT$$

Except for the excluded volume, b', this corresponds to the perfect gas equation. The number of single and double molecules are determined by Eq. (14) with the activity coefficients set equal to unity. If we take V to be the molal volume, (regarding the substance to be composed of monomers) then

$$n_1 + 2n_2 = 1$$

because the concept of molal volume is based on the notion that all the molecules are single. From the last equation and Eq. (14), it follows that

$$n_2 = \frac{V}{8 K(T)} \left[\left\{ 1 + \frac{4 K(T)}{V} \right\} - \left\{ 1 + \frac{8 K(T)}{V} \right\}^{1/2} \right]$$

For large volumes, expanding the right side of this equation in powers of $1/V$ gives

$$n_2 = K(T)/V - 4 \left[K(T)/V \right]^2 + \ldots$$

Thus

$$PV/RT = [1 - n_2][1 - b'/V]^{-1}$$

$$= [1 - K/V + 4(K/V)^2 - \ldots][1 + b'/V + (b'/V)^2 + \ldots]$$

$$= 1 + (b' - K)/V + (b'^2 - b'K + 4K^2)/V^2 + \ldots$$

so that the second virial coefficient becomes

$$B(T) = b' - \chi(T)$$

The excluded volume, b', can then be identified with $B_f(T)$. Ordinarily, $B_f(T)$ is positive corresponding to positive values of the excluded volume. However, at low temperatures $B_f(T)$, and therefore the excluded volume, becomes negative! Thus, this simplified analysis shows the limitations of the concept of excluded volume.

We will now proceed with the derivations of the relations for $B_f(T)$, $B_b(T)$, and $B_m(T)$. Actually these relations were obtained when we tried to extend, to molecules obeying an arbitrary intermolecular potential, a result which R. Byron Bird[10] has obtained for molecules obeying a monotonically varying intermolecular potential. Bird had used quantum mechanical arguments to express the second virial coefficient in terms of the angle of deflection of the trajectories. For monotonically varying intermolecular potentials, no bound or metastable double molecules can exist. Our results, obtained by classical mechanical arguments, agree with Bird's for this special type of potential.

II. BIRD'S DERIVATION OF THE SECOND VIRIAL COEFFICIENT FOR MONOTONICALLY VARYING INTERMOLECULAR POTENTIALS[10]:

The quantum mechanical expression for the second virial coefficient of a gas of spherically symmetric particles in the case where the potential is monotonically decreasing with increasing separation of the particles is[11]

$$B(T) = \pm 2^{-5/2} N \lambda^3 - 2^{3/2} N \lambda^3 \sum_{\ell} (2\ell + 1) \int_0^\infty e^{-\hbar^2 \kappa^2 / 2\mu kT} \left[\frac{1}{\kappa} \frac{d\eta_\ell(\kappa)}{d\kappa} \right] d\kappa \quad (19)$$

where $\eta_\ell(\kappa)$ is the phase shift and $\kappa^2 = 2\mu K/\hbar^2$. In the case of Fermi-Dirac statistics, the plus sign is used and the sum over ℓ includes only odd values of ℓ. For Bose-Einstein statistics, the minus sign applies, and the summation is over even values of ℓ. In the case of Boltzmann statistics, $B(T)$ is the average of the Fermi-Dirac and Bose-Einstein results. Thus,

$$B(T) = -2^{1/2} N \lambda^3 \sum_{\ell} (2\ell + 1) \int_0^\infty e^{-\hbar^2 \kappa^2 / 2\mu kT} \left[\frac{1}{\kappa} \frac{d\eta_\ell(\kappa)}{d\kappa} \right] d\kappa \quad (20)$$

where the summation now extends over all values of ℓ.

To obtain the classical mechanical expression which corresponds to Eq. (20), the following steps are carried out: (1) The integral in Eq. (20) is integrated by parts. Use is made of the fact that $\eta_\ell(0) = 0$. (2) The sum over ℓ is replaced by an integration over ℓ. The result is –

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[10] Reference 3, M.T.G.L., p. 51. We wish to thank R.B. Bird for making available his unpublished notes giving his derivation.

[11] Reference 3, M.T.G.L., p. 409.

$$B(T) = -2^{1/2} N \Lambda^3 \pi^{-2} \int_0^\infty d\varkappa\, \varkappa\, e^{-\varkappa^2 \Lambda^2/2\pi} \int_0^\infty d\ell (2\ell+1) \eta_\ell(\varkappa) \qquad (21)$$

Let

$$\hbar^2 \left[\ell(\ell+1)\right]^{1/2} = \mu g b \qquad (22)$$

$$\hbar \varkappa = \mu g \qquad (23)$$

Through the use of the W.K.B. method, it is known that to the first approximation[12],

$$\chi(b,g) = \frac{2}{\varkappa} \frac{\partial \eta_\ell}{\partial b} \qquad (24)$$

Eq. (24) becomes correct in t'e limit of large values of K or ℓ where the correspondence principle requires quantum and classical mechanical results to be the same. It should be noted that Eq. (24) is only valid if there is only one turning point, and the intermolecular potential is monotonically decreasing with increasing separation of the particles. Integration of Eq. (24) gives

$$\eta_\ell = -\frac{\varkappa}{2} \int_b^\infty \chi(b', g)\, db' \qquad (25)$$

When the equation $(2\ell + 1)d\ell = 2\varkappa^2 bdb$ is used, and the order of integration over b and b' is changed, Eq. (21) becomes

$$B(T) = 2N\pi^{1/2}(\Lambda T)^{-5/2} \int_0^\infty e^{-K/\Lambda T} K^{3/2} \left[\int_0^\infty \chi b\, db\right] dK \qquad (26)$$

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[12] Reference 3, M.T.G. L., Section 10.3b, p. 687.

This is the equation Bird obtained and is valid in classical mechanics if the potential is monotonic decreasing with increasing sepatation of the interacting particles. Below Eq. (45), it will be shown by strictly classical mechanical arguments that when the potential is monotonic, Eq. (26) is an alternate means of writing the more usual expression for the second virial coefficient, i.e. Eq. (2).

III. DERIVATION OF THE SECOND VIRIAL COEFFICIENT FOR ARBITRARY INTERMOLECULAR POTENTIALS IN TERMS OF THE DOUBLE MOLECULES AND COLLISION PROCESSES:

In order to investigate the contributions to the second virial coefficient from the bound and metastably bound double molecules, it is of interest to relate

$$B'(T) = 2N\pi^{1/2}(kT)^{-7/2}\int_0^\infty e^{-K/kT} K^{3/2}\left[\int_0^\infty \chi b^2 db\right] dK \tag{27}$$

to $B(T)$ as given by Eq. (2) for the case where the potential is not necessarily monotonic. Only in the case of the monotonic potential is $B'(T) = B(T)$.

The integral, $\int_0^\infty \chi b^2 db$, is found by taking the limit of $\int_0^{b_1} \chi b^2 db$ as b_1 approaches infinity. Let us define r_1 as the value of r_m corresponding to b_1 and the given value of K. If b_1 is sufficiently large, then r_1 is very nearly equal to b_1 irrespective of the value of K. Using Eq. (5) and the definition

$$G(b, r) = b^2 r^{-2}\left[1 - \phi(r)/K - b^2/r^2\right]^{-\frac{1}{2}}, \quad \text{we obtain}$$

$$\int_0^{b_1} \chi b^2 db = \pi b_1^3/3 \quad - \int_0^{b_1^2}\int_{r_m}^\infty G(b,r) dr db^2 \tag{28}$$

If the integration over r is performed last, Eq. (23) becomes

$$\int_0^{b_1} \chi b^2 db = \pi b_1^3/3 \quad - \int_{r_e(K)}^{r_t(K)} dr \int_0^{r^2[1-\frac{\phi(r)}{K}]} G(b,r) db^2$$

$$- \int_{r_e(K)}^{r_t(K)} dr \int_0^{b_1^2} G(b,r) db^2 \quad - \int_{r_h(K)}^{r_1} dr \int_0^{r^2[1-\frac{\phi(r)}{K}]} G(b,r) db^2$$

$$- \int_0^{b_1^2} db^2 \int_{r_1}^\infty G(b,r) dr \tag{29}$$

When use is made of the fact that

$$\int G(b,r)db^2 = -2\left[\frac{2}{3}r^2\left(1-\frac{\phi(r)}{K}-\frac{b^2}{r^2}\right)^{3/2} + b^2\left(1-\frac{\phi(r)}{K}-\frac{b^2}{r^2}\right)^{1/2}\right] \tag{30}$$

and some of the resulting terms are combined into one integral, Eq. (29) can be written as

$$\int_0^{b_1}\chi b^2 db = \pi b_1^3/3 \;-\; \frac{4}{3}\int_{r_0(K)}^{r_1}r^2\left[1-\frac{\phi(r)}{K}\right]^{3/2}dr$$

$$+2K^{-3/2}C(K) \;-\; \int_0^{b_1^2}db^2\int_{r_1}^{\infty}G(b,r)dr \tag{31}$$

where

$$C(K) =$$

$$\int_{r_f(K)}^{r_h(K)}\left[\frac{2}{3}r^2\left(K-\phi(r)-\frac{Kb_f^2}{r^2}\right)^{3/2} - Kb_f^2\left(K-\phi(r)-\frac{Kb_f^2}{r^2}\right)^{1/2}\right]dr \tag{32}$$

The last integral in Eq. (31) will be evaluated in the limit that r_1 (or b_1) $\rightarrow \infty$. Let

$$J = \int_0^{b_1^2}db^2\int_{r_1}^{\infty}G(b,r)dr$$

$$= \underbrace{\int_{b^2=0}^{b^2=r_1^2}\int_{r_1}^{\infty}}_{\text{I}} + \underbrace{\int_{b^2=r_1^2}^{b^2=b_1^2}\int_{r_1}^{b_1}}_{\text{II}} + \underbrace{\int_{b^2=r_1^2}^{b^2=b_1^2}\int_{b_1}^{\infty}}_{\text{III}} \tag{33}$$

First, an upper limit for J will be calculated, and this will be shown to be equal to the lower limit for J as $r_1 \rightarrow \infty$.

$$I = 2\int_0^{r_1} b^2 db \int_{r_1}^{\infty} br^{-2}\left[1 - \frac{\phi(r)}{K} - \frac{b^2}{r^2}\right]^{-1/2} dr$$

If the positive quantity $-\phi(r)/K$ is neglected, an upper limit for I is obtained. Since

$$\int_{r_1}^{\infty} br^{-2}\left(1 - \frac{b^2}{r^2}\right)^{-1/2} dr = \int_0^{b/r_1}(1-x^2)^{-1/2} dx = \sin^{-1}(b/r_1) ,$$

$$I_{max} = 2\int_0^{r_1} b^2 \sin^{-1}(b/r_1)\, db = 2r_1^3(\pi/6 - 2/9) \tag{34}$$

Similarly,

$$III_{max} = 2\int_{r_1}^{b_1} b^2 \sin^{-1}(b/b_1)\, db =$$

$$2b_1^3\left[\pi/6 - (1/3)(r_1/b_1)^3 \sin^{-1}(r_1/b_1) - (1/9)\{(r_1/b_1)^2 + 2\}\{1 - (r_1/b_1)^2\}^{1/2}\right] \tag{35}$$

Use of Eq. (30) gives

$$II = 2\int_{r_1}^{b_1} r^2\left[\begin{array}{c}\frac{1}{3}\left[(1 - \frac{\phi(r)}{K} - \frac{r_1^2}{r^2})^{3/2} - (1 - \frac{\phi(r)}{K} - \frac{b_1^2}{r^2})^{3/2}\right] \\ -(\frac{b_1^2}{r^2})(1 - \frac{\phi(r)}{K} - \frac{b_1^2}{r^2})^{1/2} + (\frac{r_1^2}{r^2})(1 - \frac{\phi(r)}{K} - \frac{r_1^2}{r^2})^{1/2}\end{array}\right] dr \tag{36}$$

If the negative terms of Eq. (30) are neglected and $-\phi(r)/K$ is replaced by the larger quantity, $-\phi(r_1)/K$, one finds that

$$II_{max} = 2\int_{r_1}^{b_1} r^2\left[\frac{2}{3}(1 - \frac{\phi(r_1)}{K})^{3/2} + (\frac{r_1^2}{r^2})(1 - \frac{\phi(r_1)}{K})^{1/2}\right] dr$$

$$= \frac{4}{9}(1 - \frac{\phi(r_1)}{K})^{3/2}(b_1^3 - r_1^3) + 2r_1^3(1 - \frac{\phi(r_1)}{K})^{1/2}(b_1 - r_1) \tag{37}$$

One finds III_{max} and II_{max} approach zero as $r_1 \to \infty$. In the case of II_{max}, the assumption must be made that

$$\lim_{r \to \infty} r^3 \phi(r) = 0 \tag{38}$$

Thus,

$$\lim_{r_1 \to \infty} J_{max} = \pi r_1^3/3 - 4r_1^3/9 \tag{39}$$

A lower limit for J is found by replacing $-\phi(r)/K$ in Eq. (33) by the larger quantity $-\phi(r_1)/K$.

$$J_{min} = 2\int_0^{b_1} b^2 \, db \int_{r_1}^{\infty} br^{-2}\left[1 - \frac{\phi(r_1)}{K} - \frac{b^2}{r^2}\right]^{-1/2} dr = 2r_1^3\left[1 - \frac{\phi(r_1)}{K}\right]^{3/2}\left[\frac{\pi}{6} - \frac{2}{9}\right] \tag{40}$$

$$\lim_{r_1 \to \infty} J_{min} = \pi r_1^3/3 - 4r_1^3/9 \tag{41}$$

Eqs. (39) and (41) show that $\lim_{r_1 \to \infty} J = \pi r_1^3/3 - 4r_1^3/9$. Eq. (31) becomes (on taking the limit $b_1 \to \infty$)

$$\lim_{b_1 \to \infty} \int_0^{b_1} \chi b^2 \, db = \lim_{b_1 \to \infty}\left[\begin{array}{l} \pi b_1^3/3 - \pi r_1^3/3 + 4r_1^3/9 \\[2mm] - \frac{4}{3}\int_{r_0(K)}^{r_1} r^2\left[1 - \frac{\phi(r)}{K}\right]^{3/2} dr + 2K^{-3/2}C(K) \end{array}\right]$$

$$= \lim_{b_1 \to \infty}\left\{\frac{4[r_0(K)]^3}{9} - \frac{4}{3}\int_{r_0(K)}^{r_1} r^2\left[\left(1 - \frac{\phi(r)}{K}\right)^{3/2} - 1\right] dr\right\} + 2K^{-3/2}C(K) \tag{42}$$

Thus

$$\int_0^{\infty} \chi b^2 \, db = \frac{4[r_0(K)]^3}{9} - \frac{4}{3}\int_{r_0(K)}^{\infty} r^2\left[\left(1 - \frac{\phi(r)}{K}\right)^{3/2} - 1\right] dr + 2K^{-3/2}C(K) \tag{43}$$

In both Eqs. (42) and (43) use has been made of

$b_1 = r_1(1 - \phi(r_1)/K)^{\frac{1}{2}}$ and $\lim_{b_1 \to \infty} r_1 = b_1$.

Therefore,

$$B'(T) = \frac{2N\pi^{1/2}}{(kT)^{5/2}} \int_0^\infty dK\, e^{-K/kT} K^{3/2} \left\{ \frac{4[r_0(K)]^3}{9} - \frac{4}{3}\int_{\zeta(K)}^\infty r^2\left[\left(1-\frac{\phi(r)}{K}\right)^{3/2} - 1\right]dr + 2K^{-3/2}C(K)\right\} \quad (44)$$

It is desirable to perform the integration over r in Eq. (44) after the integration over K. Fig. 5 shows the region of integration. The distance of closest approach when $\phi_{\text{eff}} = \phi(r)$ ($L = 0$ in Eq. (7)) is σ when $K = 0$.

$$\int_0^\infty dK \int_{\zeta(K)}^\infty dr = \int_0^\sigma dr \int_{\phi(r)}^\infty dK + \int_\sigma^\infty dr \int_0^\infty dK \quad (45)$$

In the case of monotonic decreasing potentials, $C(K)$ is zero because $r_f(K) = r_h(K)$ for all values of K. Also, in this case, Eq. (45) would be

$$\int_0^\infty dK \int_{\zeta(K)}^\infty dr = \int_0^\infty dr \int_{\phi(r)}^\infty dK$$

because $\sigma = \infty$. After some manipulation, it is found that

$$\int_0^\infty \int_{\phi(r)}^\infty r^2 \left([K-\phi(r)]^{3/2} - K^{3/2}\right) e^{-K/kT}\, dK\, dr$$

$$= \frac{3}{4}\pi^{1/2}(kT)^{5/2}\int_0^\infty \left[e^{-\phi(r)/kT} - 1\right]r^2\, dr + \frac{1}{3}\int_0^\infty [\zeta(K)]^3\, e^{-K/kT} K^{3/2}\, dK$$

so that Eq. (44) is identical with Eq. (2). Thus, the validity of Eq. (26) in classical mechanics is demonstrated without the use of quantum mechanics.

When Eq. (45) is used, Eq. (44) becomes
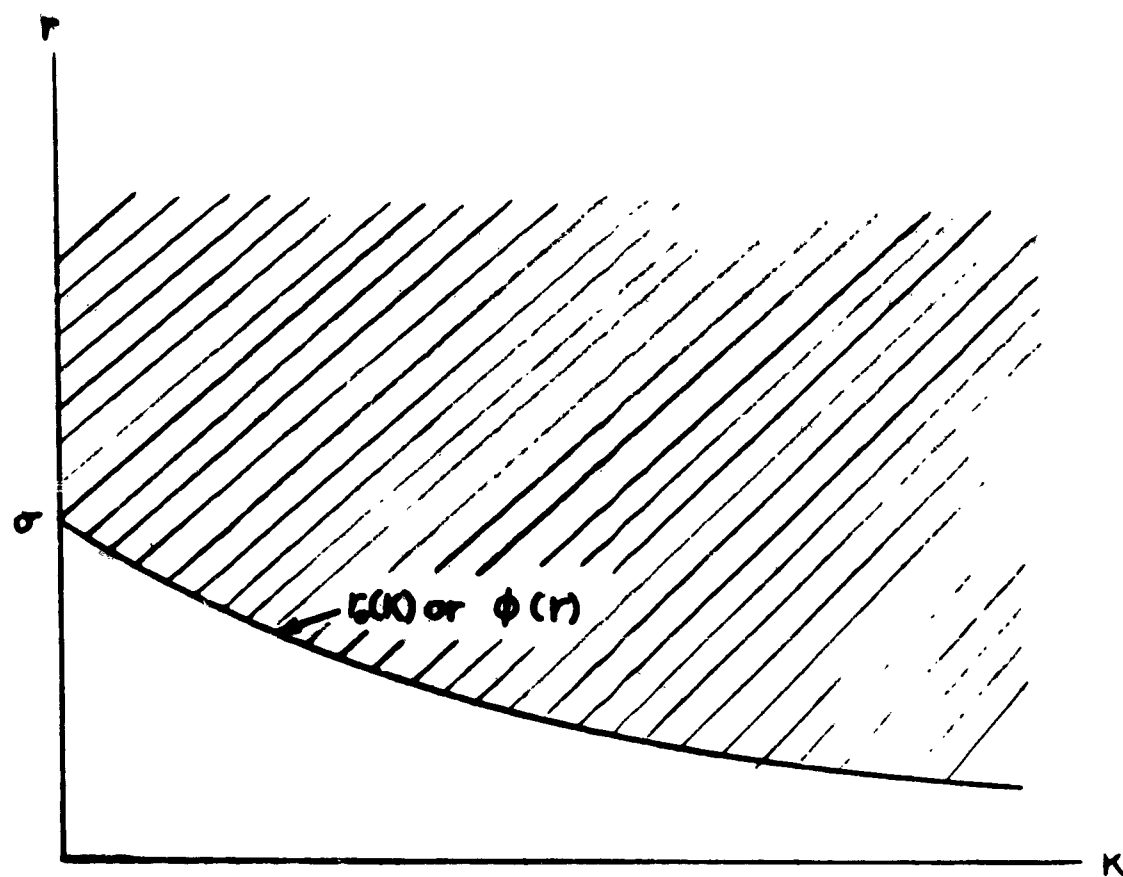
Fig. 5. The cross-hatched area indicates the region of
integration in Eq. (44).

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$$B'(T) = \frac{2N\pi^{1/2}}{(kT)^{5/2}}\left[\frac{4}{9}\int_0^\infty e^{-K/kT}K^{3/2}[\zeta(K)]^3 dK - \frac{4}{3}\int_0^\sigma\int_{\phi_m}^\infty r^2[K-\phi(r)]^{3/2}e^{-K/kT}dKdr\right.$$

$$+ \frac{4}{3}\int_0^\sigma\int_{\phi(r)}^\infty r^2 e^{-K/kT}K^{3/2}dKdr - \frac{4}{3}\int_\sigma^\infty\int_0^\infty r^2[(K-\phi(r))^{3/2}-K^{3/2}]dKdr$$

$$\left.+ 2\int_0^{K_c} C(K)e^{-K/kT}dK\right] \qquad (46)$$

In the last term of Eq. (46), the upper limit for the integration over K is K_c because for values of K above K_c, $r_f(K) = r_h(K)$.

Then, by using

$$\int_{\phi(r)}^\infty [K-\phi(r)]^{3/2} e^{-K/kT}dK = \frac{3}{4}\pi^{1/2}(kT)^{5/2}e^{-\phi(r)/kT}$$

$$\int_0^\sigma\int_{\phi_m}^\infty r^2 e^{-K/kT}K^{3/2}dKdr = \frac{3}{4}\pi^{1/2}(kT)^{5/2}\int_0^\sigma r^2 dr - \frac{1}{3}\int_0^\infty e^{-K/kT}K^{3/2}[\zeta(K)]^3 dK$$

$$\int_0^\infty K^{3/2}e^{-K/kT}dK = \frac{3}{4}\pi^{1/2}(kT)^{5/2}$$

and

$$\int_0^\infty [K-\phi(r)]^{3/2} e^{-K/kT}dK = \frac{3}{4}\pi^{1/2}(kT)^{5/2}e^{-\phi(r)/kT} - (kT)^{5/2}e^{-\phi(r)/kT}\Gamma\left(\frac{5}{2},-\frac{\phi(r)}{kT}\right)$$

one finds

$$B'(T) = 2N\pi^{1/2}(kT)^{-5/2}\left[\pi^{1/2}(kT)^{5/2}\int_0^\infty r^2[1-e^{-\phi(r)/kT}]dr\right.$$

$$+ \frac{4}{3}(kT)^{5/2}\int_\sigma^\infty r^2 e^{-\phi(r)/kT}\Gamma\left(\frac{5}{2},-\frac{\phi(r)}{kT}\right)dr$$

$$\left.+ 2\int_0^{K_c} C(K)e^{-K/kT}dK\right] \qquad (47)$$

Here $\Gamma(n,x)$ is an incomplete gamma function.

It is known that the partition function for bound pairs of molecules is[13]

$$Q_{2b} = 2\pi V \Lambda^{-6} \int_\sigma^\infty r^2 e^{-\phi(r)/kT} [\Gamma(\tfrac{3}{2}, -\tfrac{\phi(r)}{kT})/\Gamma(\tfrac{3}{2})] dr$$

Thus, Eq. (11) gives

$$B_b(T) = -2N\pi \int_\sigma^\infty r^2 e^{-\phi(r)/kT} [\Gamma(\tfrac{3}{2}, -\tfrac{\phi(r)}{kT})/\Gamma(\tfrac{3}{2})] dr \qquad (48)$$

The use of Eqs. (2), (47), and (48) together with the equation

$$\Gamma(\tfrac{5}{2}, -\tfrac{\phi(r)}{kT})/\Gamma(\tfrac{5}{2}) = \Gamma(\tfrac{3}{2}, -\tfrac{\phi(r)}{kT})/\Gamma(\tfrac{3}{2}) - e^{\phi(r)/kT} [-\tfrac{\phi(r)}{kT}]^{3/2}/\Gamma(\tfrac{5}{2})$$

gives

$$B(T) = B_b(T) + B'(T) + \tfrac{8}{3}N\pi^{1/2} \int_\sigma^\infty r^2 [-\tfrac{\phi(r)}{kT}]^{3/2} dr$$

$$- \frac{4N\pi^{1/2}}{(kT)^{5/2}} \int_0^{K_c} C(K) e^{-K/kT} dK \qquad (49)$$

In order to find the contribution of the metastably bound double molecules to the second virial coefficient, we start with the equation for the partition function of two particles:

$$Q_2 = \tfrac{1}{2h^6} \int e^{-H/kT} dx\,dy\,dz\,d\theta\,d\phi\,dr\,dp_x\,dp_y\,dp_z\,dp_\theta\,dp_\phi\,dp_r$$

$$H = (p_x^2 + p_y^2 + p_z^2)/4m + (p_\theta^2 + p_\phi^2/\sin^2\theta)/mr^2 + p_r^2/m + \phi(r)$$

Here, x, y, and z refer to the cartesian coordinates of the center of mass while the other coordinates are the relative coordinates of the two molecules. If the change of variables, $P_\theta = p_\theta/(mr^2 kT)^{\frac{1}{2}}$, $P_\phi = p_\phi/(mr^2 kT)^{\frac{1}{2}}$, and $P_r = p_r/(mkT)^{\frac{1}{2}}$ is made, and the integrations over x, y, z, θ, ϕ, p_x, p_y, and p_z are carried out,

- - - - -

[13] Reference 2.

$$Q_2 = 2V\pi^{-1/2}\Lambda^{-6}\int r^2 \exp\left[-\frac{\phi(r)}{kT} - P_\theta^2 - P_\phi^2 - P_r^2\right] dr\, dP_\theta\, dP_\phi\, dP_r \qquad (50)$$

The total energy in the center of mass system is given by

$$K = kT(P_\theta^2 + P_\phi^2) + \phi(r) + kT P_r^2$$

Also,

$$(P_\theta^2 + P_\phi^2)kT = Kb^2/r^2$$

where Kb^2/r^2 is the centrifugal potential. Only the sum of the squares of P_θ and P_ϕ is important in determining the centrifugal potential, so a change to polar coordinates is made using

$$\iint dP_\theta\, dP_\phi = \pi(kT)^{-1}\int r^{-2} d(Kb^2)$$

When the variable P_r is replaced by the variable K,

$$Q_2 = V\pi^{1/2}(kT)^{-3/2}\Lambda^{-6}\int\left[K - \phi(r) - \frac{Kb^2}{r^2}\right]^{-1/2} e^{-K/kT} d(Kb^2)\, dr\, dK \qquad (51)$$

To obtain $B_m(T)$, the integration in Eq. (51) must be restricted to the regions indicated in Figs. 6a and 6b. For a fixed K, Fig. 6a shows the effective potentials for the two extreme values of Kb^2 which are allowed. The lower of these is Kb_f^2 and the upper is Kb_2^2. Fig. 6b shows the region of integration for a fixed K. The condition

$$Kb^2 = r^2[K - \phi(r)] \qquad (52)$$

is true at the turning points of motion. From its definition, Eq. (12),

$$\phi_{eff} = \phi(r) + K b_f^2 / r^2$$

$$\phi_{eff} = \phi(r) + K b_2^2 / r^2$$

Energy

K

$r_f(K)$ r' $r_h(K)$ r
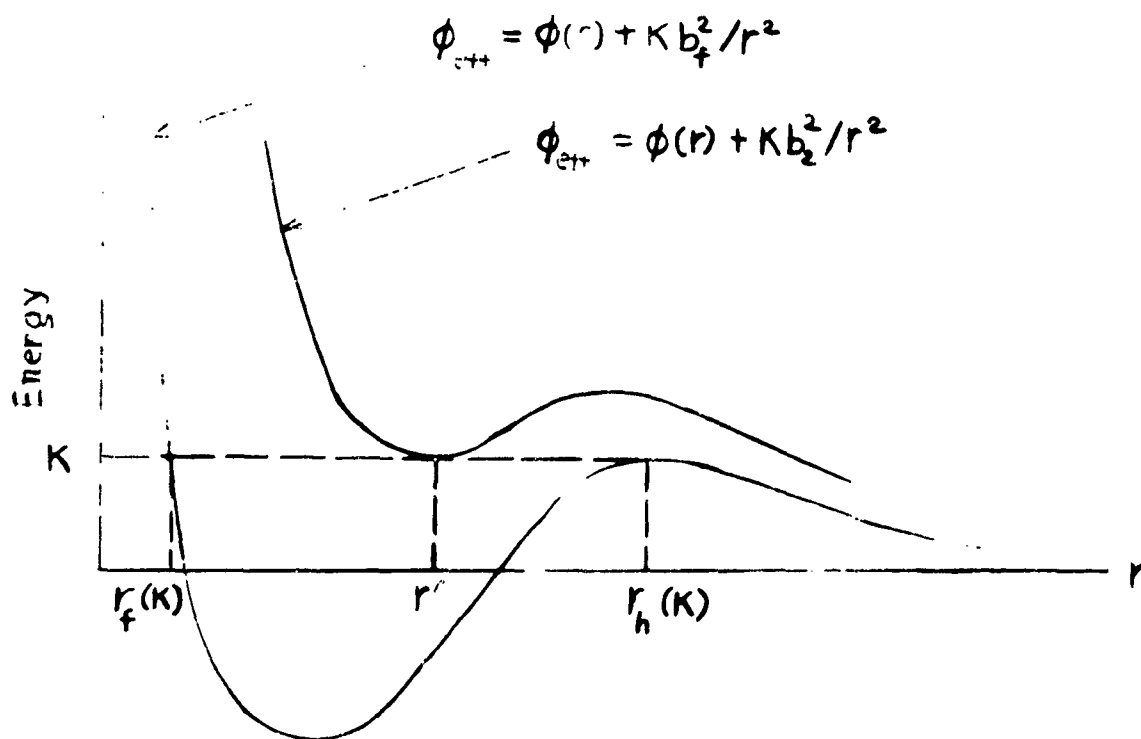
Fig. 6a.   The effective potentials when $b = b_f$ and $b = b_2$.

Kb^2

Kb_2^2

$$Kb^2 = r^2 [K - \phi(r)]$$

Kb_f^2

r_f r' r_h r
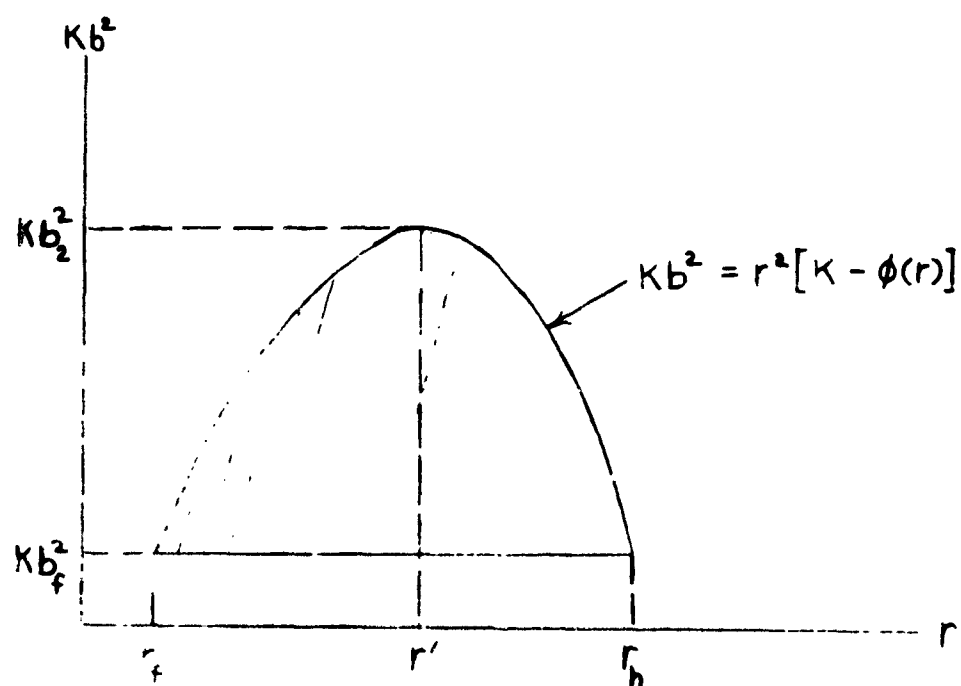
Fig. 6b.   The region of integration indicated in Eq. (53)
for a fixed value of K.

$$B_m(T) = -\frac{N\pi^{1/2}}{(kT)^{3/2}} \int_0^{K_c}\int_{\xi(K)}^{r_h(K)}\int_{Kb_f^2}^{r^2[K-\phi(r)]}\left[K-\phi(r)-\frac{Kb^2}{r^2}\right]^{-1/2}e^{-K/kT}d(Kb^2)\,dr\,dK \quad (53)$$

so that

$$B_m(T) = -\frac{2N\pi^{1/2}}{(kT)^{3/2}}\int_0^{K_c}\int_{f_\xi(K)}^{r_h(K)}r^2\left[K-\phi(r)-\frac{Kb^2}{r^2}\right]^{1/2}e^{-K/kT}\,dr\,dK \quad (54)$$

Combining Eqs. (49), (54), and (3) shows that

$$B_f(T) = B'(T) + \frac{8N\pi^{1/2}}{3(kT)^{3/2}}\int_\sigma^\infty r^2[-\phi(r)]^{3/2}\,dr$$

$$- \frac{4N\pi^{1/2}}{(kT)^{3/2}}\int_0^{K_c}C(K)\,e^{-K/kT}dK \quad - B_m(T) \quad (55)$$

Thus, the second virial coefficient has been divided into three parts. $B_b(T)$ is given by Eq. (48), $B_m(T)$ by Eq. (54), and $B_f(T)$ by Eq. (55). In the case where the potential is monotonic decreasing, all the terms except $B'(T)$ are zero and $B(T)$ is given by Eq. (26). For arbitrary potentials, $B_b(T)$ and $B_m(T)$ have to be considered in addition to $B_f(T)$. In $B_f(T)$, the terms added to $B'(T)$ are a result of the fact that there is more than one turning point (see comment below Eq. (24)).

IV. EVALUATION OF THE THREE PARTS OF THE SECOND VIRIAL
COEFFICIENT FOR SEVERAL INTERMOLECULAR POTENTIALS:

The results of the previous section will now be applied to the square well, Sutherland, and Lennard-Jones potentials. For these potentials, it is convenient to write the equations in terms of reduced variables. This also permits an easy tabulation of numerical results. Let $r^* = r/\sigma$, $b^* = b/\sigma$, $K^* = K/\epsilon$, $\phi^* = \phi/\epsilon$, $T^* = kT/\epsilon$, and $D(K^*) = (\sigma\, \epsilon^{1/2})^{-3}\, C(K)$. Thus,

$$B_b^*(T^*) = -3 \int_1^\infty r^{*2} e^{-\phi^*/T^*} \frac{\Gamma(3/2, -\phi^*/T^*)}{\Gamma(3/2)} \, dr^* \qquad (56)$$

$$B_m^*(T^*) = -3\pi^{-1/2} T^{*-3/2} \int_0^{K_c^*} M(K^*) \, e^{-K^*/T^*} dK^* \qquad (57)$$

$$M(K^*) = \int_{r_f^*(K^*)}^{r_h^*(K^*)} r^{*2} \left[K^* - \phi^*(r^*) - \frac{K^* b_f^{*2}}{r^{*2}} \right]^{1/2} dr^* \qquad (58)$$

$$B_f^*(T^*) = 3\pi^{-1/2} T^{*-5/2} \int_0^\infty e^{-K^*/T^*} K^{*3/2} \left[\int_0^\infty \chi\, b^{*2} db^* \right] dK^*$$

$$+ 4\pi^{-1/2} T^{*-3/2} \int_1^\infty r^{*2} \left[-\phi^*(r^*) \right]^{3/2} dr^* \quad - B_m^*(T^*)$$

$$- 6\pi^{-1/2} T^{*-5/2} \int_0^{K_c^*} D(K^*) \, e^{-K^*/T^*} dK^* \qquad (59)$$

$$D(K^*) = \int_{r_f^*(K^*)}^{r_h^*(K^*)} \left[\frac{2}{3} r^{*2} \left(K^* - \phi^*(r^*) - \frac{K^* b_f^{*2}}{r^{*2}} \right)^{3/2} \right.$$

$$\left. + K^* b_f^{*2} \left(K^* - \phi^*(r^*) - \frac{K^* b_f^{*2}}{r^{*2}} \right)^{1/2} \right] dr^* \qquad (60)$$

(a) The Square Well Potential.

This potential is given by

$$\phi^*(r^*) = \infty \qquad\qquad r^* < 1$$
$$\phi^*(r^*) = -1 \qquad\qquad 1 < r^* < R$$
$$\phi^*(r^*) = 0 \qquad\qquad r^* > R$$

The expression for $B_b^*(T^*)$ is given by Eq. (56),

$$B_b^*(T^*) = 2\pi^{-1/2}(1-R^3)\,\Gamma(3/2, T^{*-1})\,e^{T^{*-1}} \qquad (61)$$

Because of the discontinuity in the potential at $r^* = R$, some special features arise. In the integral for $B_m^*(T^*)$, two cases occur depending on the value of K^*. The separation of the two cases occurs when

$$\phi_{eff}^*(1) = K^* b_f^{*2}/R^2$$

or

$$K^* b_f^{*2} - 1 = K^* b_f^{*2}/R^2$$

Since $b_f^{*2} = R^2$, it follows that

$$K^* = (R^2 - 1)^{-1}$$

In case I, $K^* < (R^2 - 1)^{-1}$ and $r_f^*(K^*) = 1$. In case II, $K^* > (R^2 - 1)^{-1}$ and $r_f^*(K^*) > 1$. Figs. 7a and 7b show the two cases. Also, because of the discontinuity of the potential at $r^* = R$, it follows that K_c^* is infinite instead of finite as is the case for smoothly varying potentials. To find $B_m^*(T^*)$, the integration limits for $M(K^*)$ must first be determined from Eq. (52). For case I, one obtains $r_f^*(K^*) = 1$ and $r_h^*(K^*) = R$. For case II, $r_f^*(K^*) = R[K^*/(K^*+1)]^{\frac{1}{2}}$ and $r_h^*(K^*) = R$. The integration over r^* gives

$$B_m^*(T^*) = \frac{-1}{\pi^{1/2}T^{*3/2}}\left\{ R^3 \int_0^\infty \frac{e^{-K^*/T^*}}{(K^*+1)}dK^* - \int_0^{(R^2-1)^{-1}} \frac{[1-(R^2-1)K^*]^{3/2}e^{-K^*/T^*}}{(K^*+1)}dK^* \right\} \quad (62)$$

The first integral in Eq. (62) is easily integrated in terms of the exponential integral
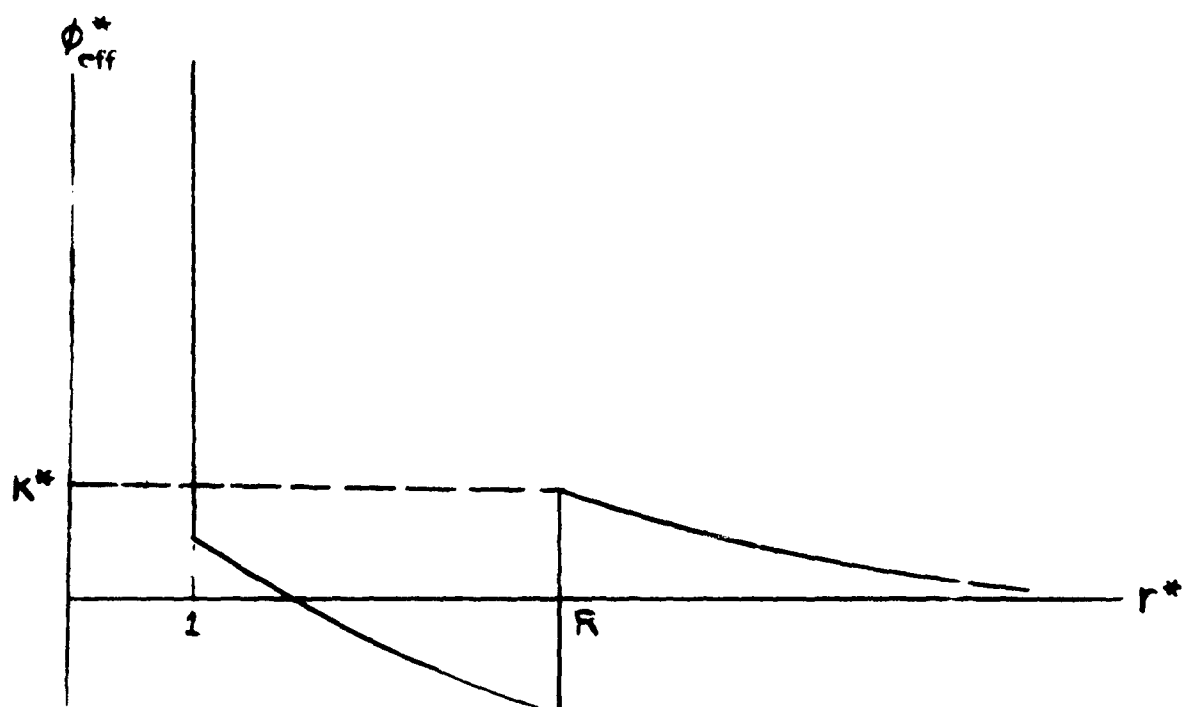
Fig. 7a. ϕ^*_{eff} versus r^* for the Square Well Potential.

Case I: $K^* < (R^2 - 1)^{-1}$ and $r^*_f(K^*) = 1$.
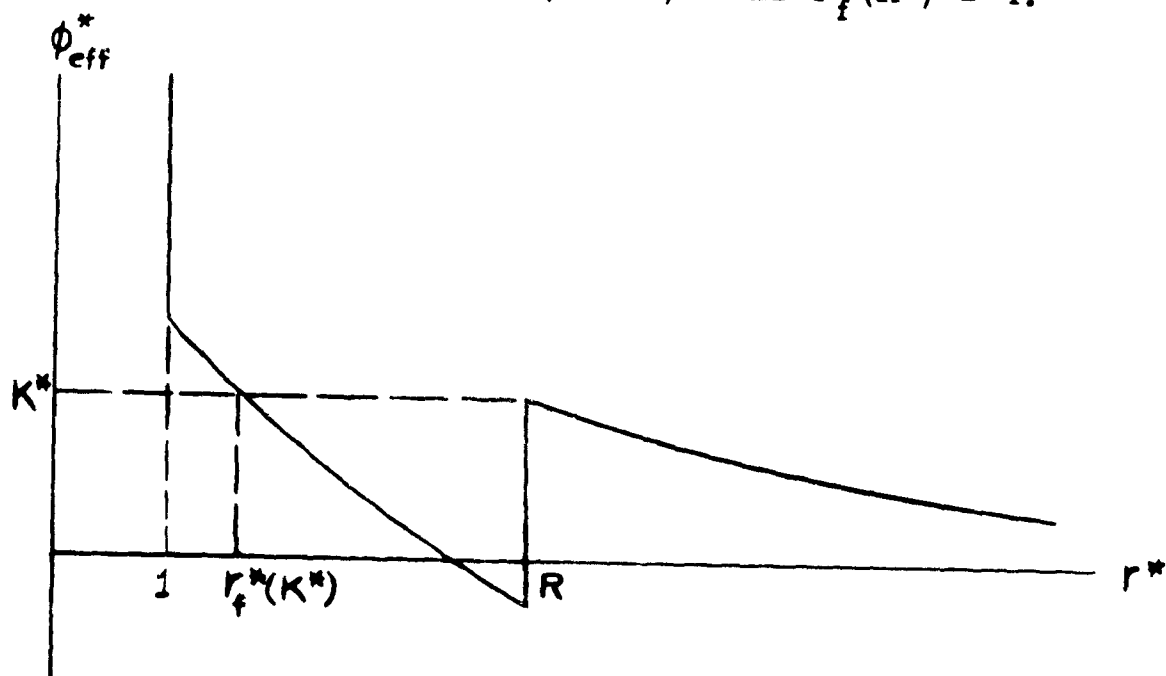
Fig. 7b. ϕ^*_{eff} versus r^* for the Square Well Potential.

Case II. $K^* > (R^2 - 1)^{-1}$ and $r^*_f(K^*) > 1$.

$$E_i(-t) = -\int_t^\infty \frac{e^{-x}dx}{x} \tag{63}$$

The second integral in Eq. (62) can be evaluated by making a change in variables to $y = [1 - (R^2 - 1)K^*]/R^2$ and then expanding the exponential term. Thus

$$B_m^*(T^*) = \frac{-R^3 e^{T^{*-1}}}{\pi^{1/2} T^{*3/2}}\left[-E_i(-T^{*-1}) + \frac{2}{3R^3} + \frac{2}{R} - \ln\frac{R+1}{R-1} - \sum_{n=1}^{\infty}\left(\frac{-R^2}{R^2-1}\right)^n \frac{B_{1/R^2}(5/2,n)}{n!\,T^{*n}}\right] \tag{64}$$

where

$$B_{1/R^2}(5/2,n) = \int_0^{R^{-2}} x^{3/2}(1-x)^{n-1}dx \tag{65}$$

is an incomplete beta function.

The equations for χ, to be used in Eq. (59) are given by Holleran and Hulburt[14]. The integrations in Eq. (59) can be carried out to give

$$B_+^*(T^*) = 1 - (R^3-1)(e^{T^{*-1}}-1) - B_s^*(T^*) - B_m^*(T^*) \tag{66}$$

As a check on the work, Eq. (3) (in its reduced form) can be used in Eq. (66). When this is done, one obtains the well known result for the second virial coefficient of particles interacting with a square well potential.

Table I gives the values of the coefficients $\left(\frac{-R^2}{R^2-1}\right)^n \frac{B_{1/R^2}(5/2,n)}{n!}$ which appear in Eq. (64). The various contributions to the second virial coefficient are shown in Table II for three values of the parameter R. Fig. 8 is a graph for the case $R = 1.5$.

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[14] E. M. Holleran and H. M. Hulburt, J. Chem. Phys. 19, 232 (1951).

Table I. The Square Well Potential Coefficients

$$\left[\frac{-R^2}{R^2-1}\right]^n \frac{B_{1/a^2}(5/2, n)}{n!} \quad \text{Which}$$

Occur in Eq. (64)   for $B_m^*(T^*)$.

n \ R	1.5	1.7	1.9
1	-9.48146×10^{-2}	-4.30777×10^{-2}	-2.23438×10^{-2}
2	5.82435×10^{-2}	2.47950×10^{-2}	1.23950×10^{-2}
3	-2.43107×10^{-2}	-9.60556×10^{-3}	-4.60869×10^{-3}
4	7.76289×10^{-3}	2.81876×10^{-3}	1.29243×10^{-3}
5	-2.02366×10^{-3}	-6.68550×10^{-4}	-2.91628×10^{-4}
6	4.48630×10^{-4}	1.33531×10^{-4}	5.51624×10^{-5}
7	-8.69652×10^{-5}	-2.31036×10^{-5}	-8.99779×10^{-6}
8	1.50368×10^{-5}	3.53503×10^{-6}	1.29210×10^{-6}

Table II. Contributions to the Second Virial Coefficient for the Square Well Potential

R = 1.5

T^*	B_s^*	B_m^*	B_f^*	B^*
.5	-12.960	-1.61	.40	-14.1740
1.0	- 2.76051	-1.01230	.69190	- 3.08091
1.5	- 1.28954	- .732699	.77137	- 1.25087
2.0	- .778239	- .573461	.819988	- .540712
3.0	- .394385	- .396699	.853896	+ .060422
4.0	- .247345	- .301379	.874165	.325441
5.0	- .173346	- .241488	.889002	.474168
10.0	- .0588232	- .116675	.925717	.750219

R = 1.7

T^*	B_s^*	B_m^*	B_f^*	B^*
.5	-21.353	-2.59	-.05	-26.0004
1.0	- 4.54816	-1.56154	+.34807	- 5.72363
1.5	- 2.12461	-1.11471	.53443	- 2.70849
2.0	- 1.28221	- .869213	.61367	- 1.53845
3.0	- .649781	- .597860	.699611	- .546030
4.0	- .407521	- .451958	.748069	- .111390
5.0	- .285602	- .348132	.780364	+ .133650
10.0	- .0969159	- .173328	.858710	.588466

Table II. (Continued)

T^*	B_b^*	B_m^*	B_f^*	B^*
		$R = 1.9$		
.5	-31.972	-3.767	-.694	-36.4335
1.0	- 6.81004	-2.23688	-.02048	- 9.06740
1.5	- 3.18122	-1.59467	+.22311	- 4.55278
2.0	- 1.91987	-1.23638	.35539	- 2.80066
3.0	- .972928	-.846952	.50199	- 1.31789
4.0	- .610188	-.639072	.585158	- .664102
5.0	- .427636	-.510019	.640455	- .297200
10.0	- .145114	-.244086	.773003	+ .383803

Fig. 8. The Contributions to the Second Virial Coefficient B^*, B_b^*, B_m^*, and B_f^* for a Square-Well Potential with $R = 1.5$.
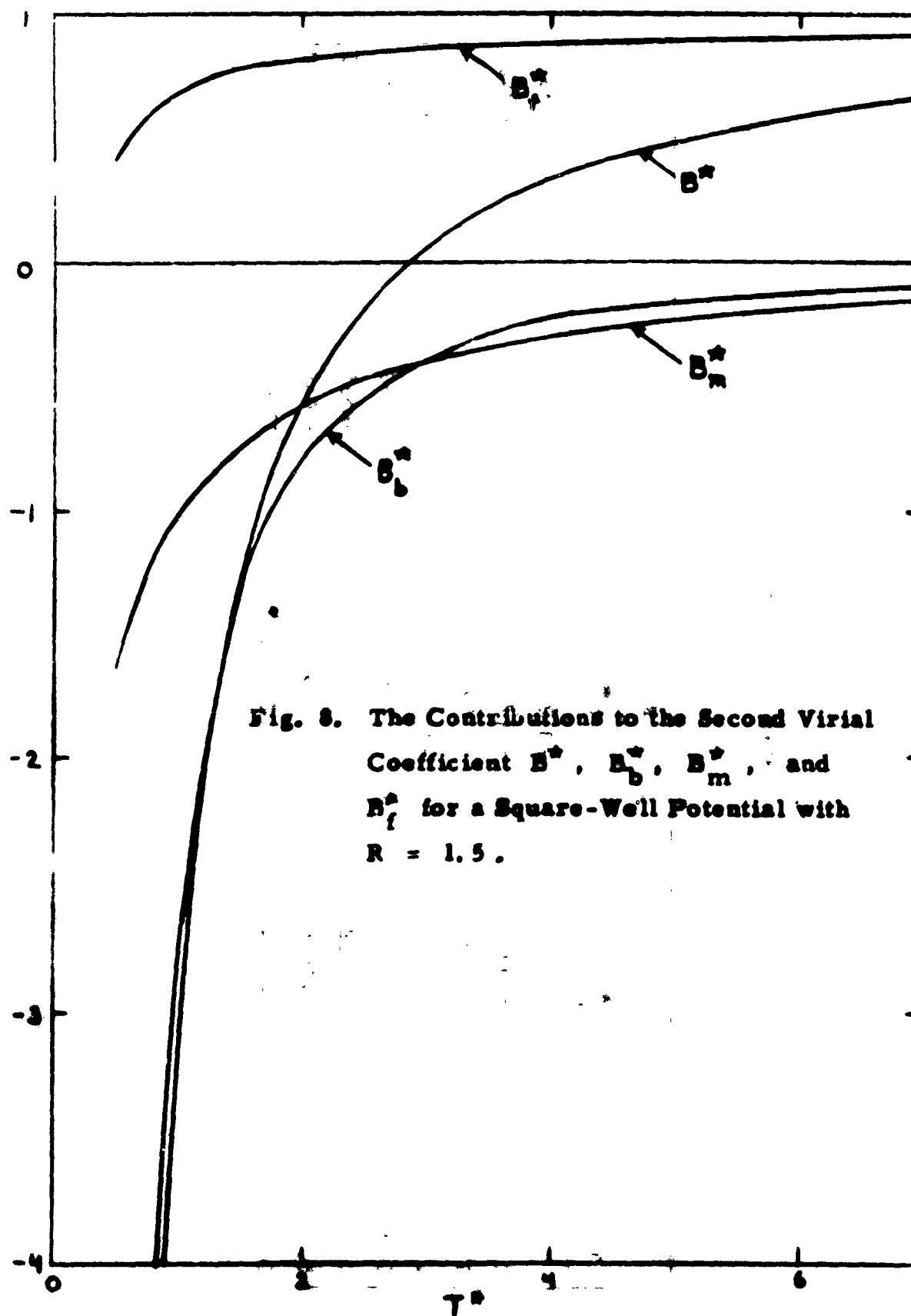
(b) The Sutherland Potential.

The potential for this model is

$$\phi^*(r^*) = \infty \qquad r^* < 1$$

$$\phi^*(r*) = -r^{*-\gamma} \qquad r^* > 1$$

The equation for $B_b^*(T^*)$ will be given as a power series in T^{*-1}. An expansion for $e^x \Gamma(3/2, x)/\Gamma(3/2)$ is first developed; this expansion will also be useful in finding $B_b^*(T^*)$ for the Lennard-Jones potential. The incomplete gamma function is a particular case of the confluent hypergeometric[15] function which is defined by

$$\Phi(a, c; x) = \sum_{n=0}^{\infty} \frac{(a)_n}{(c)_n} \frac{x^n}{n!} \tag{67}$$

where

$$(a)_0 = 1$$

$$(a)_n = a(a+1)\ldots(a+n-1) \qquad n = 1, 2, \ldots$$

Thus,

$$e^x \Gamma(3/2, x)/\Gamma(3/2) = \frac{2 x^{3/2} e^x}{3 \Gamma(3/2)} \Phi(3/2, 5/2; -x)$$

$$= \frac{2 x^{3/2}}{3 \Gamma(3/2)} \Phi(1, 5/2; x)$$

$$= \frac{8 x^{3/2}}{\pi^{1/2}} \sum_{n=0}^{\infty} \frac{4^n (n+1)! \, x^n}{(2n+3)!} \tag{68}$$

Here, the second step follows from Kummer's transformation and the third step from Eq. (67).

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[15] A. Erdelyi, "Higher Transcendental Functions", Vol. I, Bateman Manuscript Project, (McGraw-Hill, 1953). Ch. VI of this book has a summary of all the properties of the confluent hypergeometric function used in this paper. It also has information on the Whittaker functions which are introduced in the discussion of the Lennard-Jones potential.

If the expansion, Eq. (68), is used in Eq. (56), integrals of the

form $\int_1^\infty r^{*2-\gamma(n+1)} dr^* = \frac{2}{2\gamma n + 3\gamma - 6}$ result; Eq. (56) becomes

$$B_b^*(T^*) = \frac{-48}{\pi^{1/2} T^{*3/2}} \sum_{n=0}^{\infty} \frac{4^n (n+1)!}{(2n+3)!(2\gamma n + 3\gamma - 6) T^{*n}} \tag{69}$$

Eq. (69) is valid if $\gamma > 2$. It will be shown below that $B_m^*(T^*)$ also is defined for $\gamma > 2$. This is to be contrasted with the result for the second virial coefficient for this potential which is defined only for $\gamma > 3$. The fact that B_b^* and B_m^* are defined when $\gamma > 2$ implies that an equilibrium constant for the formation of double molecules can be calculated (see Eq. (15)) for some cases where the second virial coefficient does not exist.

For the special case where $\gamma = 6$,

$$B_b^*(T^*) = \frac{-4}{\pi^{1/2} T^{*3/2}} \sum_{n=0}^{\infty} \frac{a_n}{T^{*n}} \tag{70}$$

where

$$a_n = \frac{4^n n!}{(2n+3)!} \tag{71}$$

We find that $a_0 = 1.66666 \times 10^{-1}$, $a_1 = 3.33333 \times 10^{-2}$,

$a_2 = 6.34921 \times 10^{-3}$, $a_3 = 1.05820 \times 10^{-3}$, $a_4 = 1.53920 \times 10^{-4}$,

$a_5 = 1.97334 \times 10^{-5}$, $a_6 = 2.25524 \times 10^{-6}$, and $a_7 = 2.32157 \times 10^{-7}$.

To find $B_m^*(T^*)$, one must first determine $K^* b_f^{*2}$, K_c^*, and integration limits for $M(K^*)$. From the form of the potential, it is obvious that $r_f^*(K^*) = 1$. One finds $K^* b_f^{*2} = \frac{\gamma}{2}\left(\frac{2K^*}{\gamma-2}\right)^{1-\frac{2}{\gamma}}$ and $r_h^*(K^*) = \left(\frac{\gamma-2}{2K^*}\right)^{1/\gamma}$ by solving the equations $d\phi_{eff}^*/dr^* = 0$ and $\phi_{eff}^*(r^*) = K^*$. By letting $r_f^*(K^*) = r_h^*(K^*)$, it is found that $K_c^* = \frac{\gamma-2}{2}$.

When the above equations for $K^* b_f^{*2}$, r_f^*, and r_h^* are used and the substitution $t = \left(\frac{2K^*}{\gamma-2}\right)^{1/\gamma} r^*$ is made, the integral $M(K^*)$ becomes

$$M(K^*) = \left(\frac{\gamma-2}{2K^*}\right)^{\frac{1}{\gamma}-\frac{1}{2}} \int_{\left(\frac{2K^*}{\gamma-2}\right)^{1/\gamma}}^{1} t^{2-\frac{1}{2}} \left[\frac{\gamma-2}{2} t^{\gamma} - \frac{\gamma}{2} t^{\gamma-2} + 1\right]^{1/2} dt \tag{72}$$

If $\gamma > 2$ in Eq. (72), it is easy to see that Eq. (57) gives a finite value for B_m^*. It should be noticed that the polynomial under the square root sign always has a double root at $t = 1$.

The integral of Eq. (72) can be evaluated for several choices of γ but unfortunately a different method must be used for each choice. We shall consider only the case $\gamma = 6$. When the substitution $z = t^2$ is made in Eq. (72) and $(1 - z)^2$ is factored from under the square root sign, $M(K^*)$ is easily evaluated. Thus,

$$M(K^*) = \frac{3^{1/2}}{2} - \left[1 + (4K^*)^{1/3}\right]^{1/2} + \frac{1}{6}\left[1 + (4K^*)^{1/3}\right]^{3/2}$$

$$- \coth^{-1} 3^{1/2} + \coth^{-1}\left[1 + (4K^*)^{1/3}\right]^{1/2} \tag{73}$$

On expanding the exponential in Eq. (57) and changing the integration variable to $y = \left[1 + (4K^*)^{1/3}\right]^{\frac{1}{2}}$, Eq. (57) can be integrated to give

$$B_m^*(T^*) = \frac{-3}{\pi^{1/2} T^{*3/2}} \sum_{n=0}^{\infty} \frac{C_n}{T^{*n}} \tag{74}$$

where

$$C_n = \frac{(-1)^n \, 3^{3/2}}{4^{n+1}(2n+3)(3n+3)n!}\left[-2^{3n+2} + (3n+4)\sum_{r=0}^{3n+2}\frac{(-1)^r(3n+2)!(3^{3n+3-r} - 3^{-1/2})}{(3n+2-r)! \, r! \, (6n+7-2r)!}\right] \tag{75}$$

We find $c_0 = 1.23065 \times 10^{-1}$, $c_1 = -3.75800 \times 10^{-2}$, $c_2 = 1.20161 \times 10^{-2}$, $c_3 = -3.51826 \times 10^{-3}$, $c_4 = 9.23385 \times 10^{-4}$, $c_5 = -2.1740 \times 10^{-4}$, $c_6 = 4.6196 \times 10^{-5}$, and $c_7 = -8.9247 \times 10^{-6}$.

The total reduced second virial coefficient for this potential when $\gamma = 6$ is [16]

$$B^*(T^*) = 1 - \sum_{n=1}^{\infty} \frac{d_n}{T^{*n}} \tag{76}$$

where

$$d_n = \frac{1}{(2n-1)n!} \tag{77}$$

Here, $d_1 = 1$, $d_2 = 1.66666 \times 10^{-1}$, $d_3 = 3.33333 \times 10^{-2}$, $d_4 = 5.95238 \times 10^{-3}$, $d_5 = 9.25926 \times 10^{-4}$, $d_6 = 1.26263 \times 10^{-4}$, $d_7 = 1.52625 \times 10^{-5}$, and $d_8 = 1.65344 \times 10^{-6}$.

When Eq. (3) is written in reduced form, $B_f^*(T^*)$ can be found by subtracting $B_b^*(T^*)$ and $B_m^*(T^*)$ from $B^*(T^*)$. Table III and Fig. 9 show the contributions to the second virial coefficient for the Sutherland potential with the attractive term equal to $-r^{*-6}$.

(c) The Lennard-Jones (6-12) Potential.

The equation for this potential is

$$\phi^*(r^*) = 4(r^{*-12} - r^{*-6}) \tag{78}$$

- - - - -

[16] Reference 3, M. T. G. L., p. 58. This follows from the equation given for $B(T)$ which is valid for $\gamma > 3$ after the typographical errors are corrected.

Table III. Contributions to the Second Virial Coefficient for the Sutherland
Potential with Attractive Term Proportional to r^{*-6}.

T^*	B_b^*	B_m^*	B_f^*	B^*
.5	-1.72639	-.3708	.0285	-2.0687
1.0	- .468467	-.160330	.421776	- .207021
1.5	- .235928	-.0944044	.578405	+ .248073
2.0	- .147659	-.0639647	.665388	.453764
3.0	- .0775353	-.0364020	.760773	.646836
4.0	- .0494834	-.0241972	.812719	.739038
5.0	- .0350405	-.0175614	.845659	.793057
10.0	- .0121367	-.00639199	.916828	.898299

Fig. 9. The Contributions to the Second Virial Coefficient B^*, B_u^*, B_m^*, and B_f^* for a Sutherland Potential with Attractive Term Proportional to r^{*-6}.
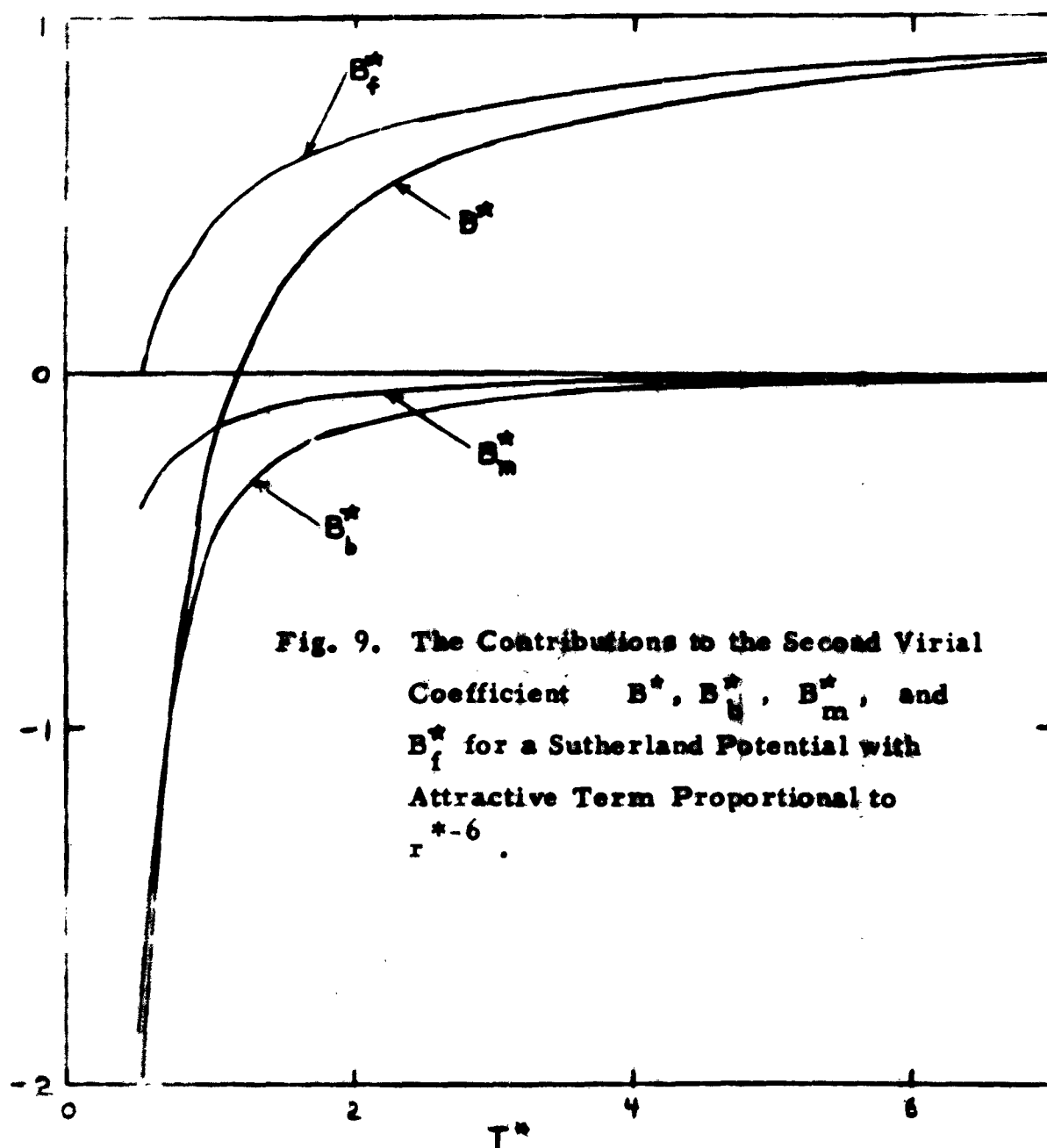
To obtain $B_b^*(T^*)$, let $x = -\phi^*(r^*)/T^*$ and use Eq. (68). In the series for $B_b^*(T^*)$, integrals of the form

$$A_n = \int_1^\infty r^{*2} \, x^{n+2k} \, dr^*$$

$$= \frac{1}{6}\left(\frac{4}{T^*}\right)^{n+2} \int_0^1 r^{*-6n}\left[1-r^{*-6}\right]^{n+2k} d(r^{*-6})$$

appear. Repeated integration by parts gives

$$A_n = \left(\frac{4}{T^*}\right)^{n+2} \frac{2^{n+1} \, n!}{6\,(2n+5)(2n+7)(2n+9)\ldots(4n+5)}$$

Thus

$$B_b^*(T^*) = \frac{-12\pi}{\pi^{1/2} \, T^{*5/2}} \sum_{n=0}^\infty e_n \qquad (79)$$

where

$$e_n = \frac{64^n \, (2n+2)! \, n!}{(4n+5)!} \qquad (80)$$

The first eight coefficients are $e_0 = 1.666666 \times 10^{-2}$,

$e_1 = 4.232804 \times 10^{-3}$, $e_2 = 9.472010 \times 10^{-4}$, $e_3 = 1.782967 \times 10^{-4}$,

$e_4 = 2.859895 \times 10^{-5}$, $e_5 = 3.978986 \times 10^{-6}$,

$e_6 = 4.878450 \times 10^{-7}$, and $e_7 = 5.341019 \times 10^{-8}$.

The integrals for either $B_m^*(T^*)$ or $B_f^*(T^*)$ must be done numerically. Of the two, the numerical integrations for $B_m^*(T^*)$ are much easier; the numerical details are described in Appendix A. When the exponential in Eq. (57) is expanded, $B_m^*(T^*)$ is found in terms of a power series in T^{*-1} with the coefficients given by

$$f_n = \frac{(-1)^n}{n!} \int_0^{0.8} K^{*n} M(K^*) \, dK^* \tag{81}$$

Thus

$$B_m^*(T^*) = \frac{-3}{\pi^{1/2} T^{*3/2}} \sum_{n=0}^{\infty} \frac{f_n}{T^{*n}} \tag{82}$$

We find that $f_0 = 2.5400 \times 10^{-1}$, $f_1 = -4.8167 \times 10^{-2}$, $f_2 = 8.2071 \times 10^{-3}$, $f_3 = -1.1886 \times 10^{-3}$, $f_4 = 1.4766 \times 10^{-4}$, $f_5 = -1.5985 \times 10^{-5}$, $f_6 = 1.5302 \times 10^{-6}$, and $f_7 = -1.3115 \times 10^{-7}$. Because of the numerical integrations, it is uncertain whether or not the f_n are correct to five significant figures.

Recently, Nosanow and Mayer[17] have shown that the reduced second virial coefficient for the Lennard-Jones (6-12) potential satisfies the differential equation

$$16 T^{*3} \frac{d^2 B^*}{dT^{*2}} + 16 T^*(1 + 2T^*) \frac{dB^*}{dT^*} + (8 + 3T^*) B^* = 0 \tag{83}$$

This equation can be solved by letting $B^* = T^{*-3/4} \tilde{\phi}(T^{*-1})$, and noticing that $\tilde{\phi}(T^{*-1})$ satisfies the differential equation of a confluent hypergeometric function[15]. Thus[18]

$$B^*(T^*) = T^{*-1/4}\left[R_1 \tilde{\phi}(-1/4, 1/2, T^{*-1}) + R_2 T^{*-1/2} \tilde{\phi}(1/4, 3/2, T^{*-1}) \right] \tag{84}$$

Here, R_1 and R_2 are constants which can be determined by comparing the series form of Eq. (84) with a result previously obtained by Lennard-Jones[19]:

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[17] L. H. Nosanow and J. E. Mayer, J. Chem. Phys. 28, 874 (1958). An error of one sign in the differential equation given by Nosanow and Mayer has been corrected in Eq. (83).

[18] An alternative method of arriving at Eq. (84) is given by L. F. Epstein and G. M. Roe, J. Chem. Phys. 19, 1320 (1951).

[19] Reference 3, M. T. G. L., p. 163.

$$R_1 = -2^{-3/2}\,\Gamma(-1/4) \tag{85}$$

$$R_2 = -2^{-1/2}\,\Gamma(1/4) \tag{86}$$

Eq. (84) can be written in terms of the Whittaker functions[15] $M_{\frac{1}{2},\,-1/4}(T^{*-1})$ and $M_{\frac{1}{2},\,1/4}(T^{*-1})$. Thus,

$$B^*(T^*) = e^{(2T^*)^{-1}}\left[R_1 M_{\frac{1}{2},-\frac{1}{4}}(T^{*-1}) + R_2 M_{\frac{1}{2},\frac{1}{4}}(T^{*-1})\right] \tag{87}$$

By using the expansions

$$M_{\frac{1}{2},-\frac{1}{4}}(T^{*-1}) = T^{*-1/4}\sum_{n=0}^{\infty}\left[\sum_{j=0}^{n}\frac{(-1)^{n-j}(-1/4)_j}{2^{n-j}(1/2)_j(n-j)!\,j!}\right]T^{*-n} \tag{88}$$

and

$$M_{\frac{1}{2},\frac{1}{4}}(T^{*-1}) = T^{*-3/4}\sum_{n=0}^{\infty}\left[\sum_{j=0}^{n}\frac{(-1)^{n-j}(1/4)_j}{2^{n-j}(3/2)_j(n-j)!\,j!}\right]T^{*-n}\ , \tag{89}$$

Eq. (87) becomes equivalent to the result given for $B^*(T^*)$ by Nosanow and Mayer except that they give recursion relations for the coefficients of T^{*-n} while Eqs. (88) and (89) show the explicit form of these coefficients.

The reduced second virial coefficient for this potential has been tabulated[20]. Thus, $B_f^*(T^*)$ is found by using Eq. (3) in its reduced form. The contributions to the second virial coefficient for the Lennard-Jones potential are shown in Table IV and Fig. 10.

With the tables given in this section, it is easy to calculate the number of bound and metastably bound double molecules in a gas if the force constants are known. If the activity coefficients are set equal

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[20] Reference 3, M.T.G.L., pp. 1114 and 1115.

Table IV. Contributions to the Second Virial Coefficient

for the Lennard-Jones (6-12) Potential

T^*	B_D^*	B_m^*	B_f^*	B^*
.4	-10.737	-1.1428	-1.919	-13.7988
.5	- 6.32600	- .87568	-1.51853	- 8.72021
.6	- 4.26718	- .69915	-1.23164	- 6.19797
.7	- 3.12140	- .57512	-1.01352	- 4.71004
.8	- 2.40909	- .48399	- .84115	- 3.73423
.9	- 1.93141	- .41467	- .70103	- 3.04711
1.0	- 1.59296	- .36049	- .58463	- 2.53808
1.25	- 1.07294	- .26664	- .36420	- 1.70378
1.50	- .784957	- .20749	- .20843	- 1.20088
1.75	- .606150	- .16739	- .09240	- .865943
2.00	- .486240	- .13873	- .09266	- .627625
2.50	- .338415	- .10104	+ .12684	- .312613
3.00	- .252803	- .077790	.215359	- .115234
4.00	- .160564	- .051296	.327277	+ .115417
5.00	- .113376	- .037042	.393762	.243344
10.00	- .039050	- .013342	.513267	.460875

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Fig. 10. Contributions to the Second Virial Coefficient B^*, B_b^*, B_m^*, and B_f^* for a Lennard-Jones (6-12) Potential.
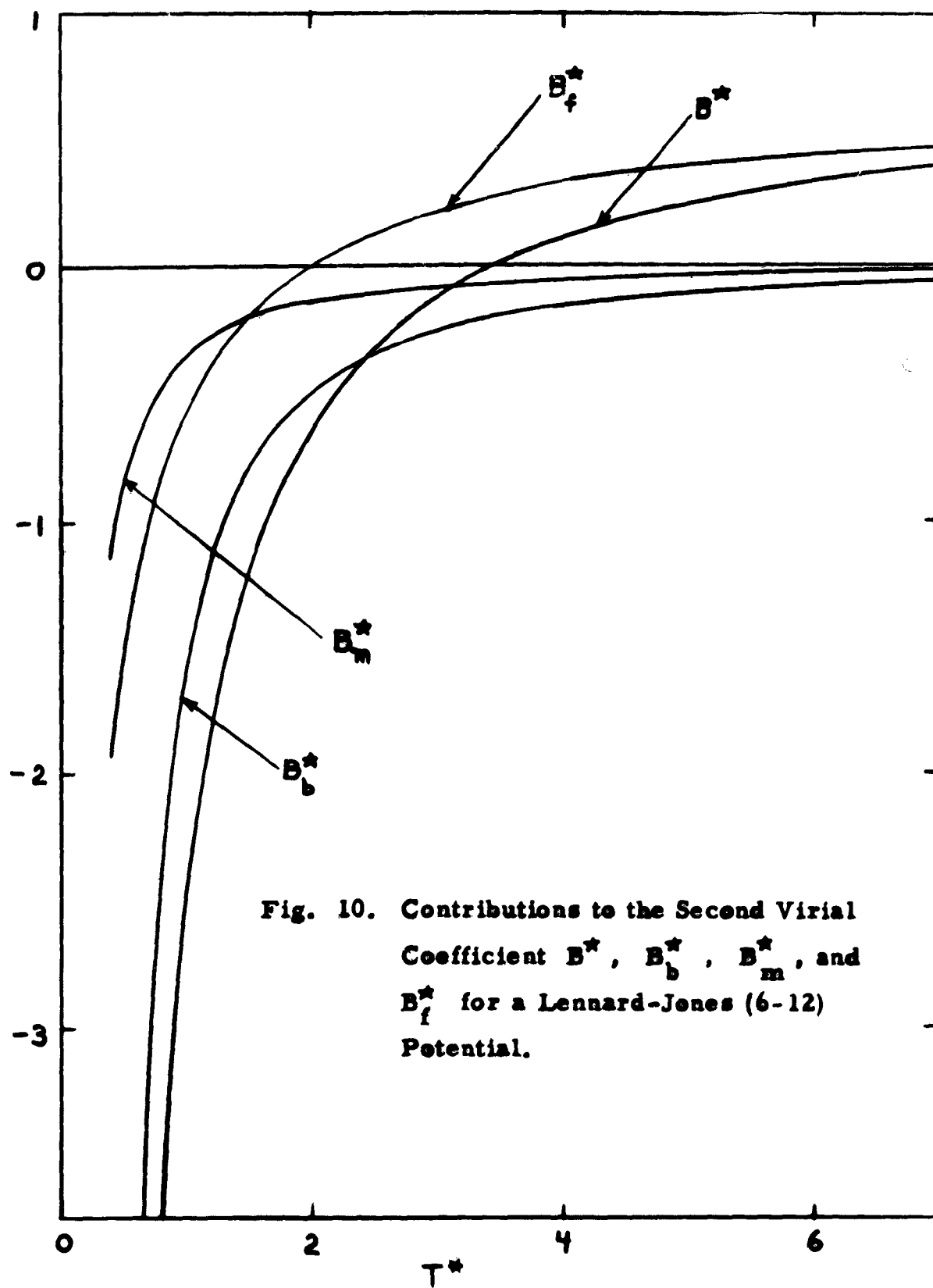
to unity in Eq. (14) and if n_1, the number of moles of single mole-
cules is replaced by n, the number of moles that would be present
if molecular association did not occur, then on using Eq. (15) the
mole fraction of double molecules is given approximately by

$$X_2 = -b_o (B_b^* + B_m^*) n / V$$

while the mole fractions of bound and metastably bound double mole-
cules are given by

$$X_{2b} = -b_o B_b^* n / V$$

$$X_{2m} = -b_o B_m^* n / V$$

As an example of the type of results to expect, we list in Table V
the mole fractions for a number of gases at several temperatures.
The calculations are for the Lennard-Jones potential and at a
concentration of 1 mole/22.4 liters (i.e. $n = 1$, $V = 2.24 \times 10^4$
c.c.).

Table V. The Mole Fraction of Dimers at a Total Concentration of 1 mole/22.4 liters Calculated Using the Lennard-Jones (6-12) Potential.[a]

Reduced Values	T^*	1.0	1.5	2.0	2.5	5.0
	X_{2b}/b_o	.0000711	.0000350	.0000217	.0000151	.00000506
	X_{2m}/b_o	.0000161	.00000926	.00000619	.00000451	.00000165
A	$T(^{\circ}K)$	120	180	240	300	599
$\epsilon/k = 119.8$	P (atmos.)	.440	.659	.879	1.10	2.19
	X_{2b}	.00354	.00175	.00108	.000753	.000252
$b_o = -49.80$	X_{2m}	.000801	.000461	.000308	.000225	.0000824
Kr	$T(^{\circ}K)$	171	257	342	428	855
$\epsilon/k = 171$	P (atmos.)	.626	.941	1.25	1.57	3.13
	X_{2b}	.00419	.00206	.00128	.000889	.000298
$b_o = -58.86$	X_{2m}	.000947	.000545	.000365	.000266	.0000974
O_2	$T(^{\circ}K)$	118	176	235	294	588
$\epsilon/k = 117.5$	P (atmos.)	.432	.645	.861	1.08	2.15
	X_{2b}	.00411	.00202	.00125	.000873	.000292
$b_o = -57.75$	X_{2m}	.000929	.000535	.000358	.000261	.0000955

(a) The force constants are from Reference 3, M.T.G.L., pp.1110-1112.

Table V. (Continued)

		100	150	200	251	501
CO	$T(^{\circ}K)$	100	150	200	251	501
$\epsilon/k = 100.2$	p (atmos.)	.366	.549	.733	.919	1.84
$b_o = 67.22$	X_{2b}	.00478	.00236	.00146	.00102	.000340
	X_{2m}	.00108	.000623	.000416	.000303	.000111
CO$_2$	$T(^{\circ}K)$	189	284	378	473	945
$\epsilon/k = 189$	p (atmos.)	.692	1.04	1.38	1.73	3.46
$b_o = 113.9$	X_{2b}	.00810	.00399	.00247	.00172	.000576
	X_{2m}	.00183	.00106	.000705	.000514	.000188
CH$_4$	$T(^{\circ}K)$	148	222	296	371	741
$\epsilon/k = 148.2$	p (atmos.)	.542	.813	1.08	1.36	2.71
$b_o = 70.16$	X_{2b}	.00499	.00246	.00152	.00106	.000355
	X_{2m}	.00113	.000650	.000435	.000317	.000116
C$_2$H$_4$	$T(^{\circ}K)$	199	299	398	498	996
$\epsilon/k = 199.2$	p (atmos.)	.729	1.10	1.46	1.82	3.65
$b_o = 116.7$	X_{2b}	.00830	.00409	.00253	.00176	.000591
	X_{2m}	.00188	.00108	.000723	.000526	.000193

Table V. (Concluded)

C₂H₆ k/k = 243 b₀ = 78	$T(^{\circ}K)$ P (atmos.) X_{2b} X_{2m}	243 .890 .00555 .00126	365 1.34 .00273 .000723	486 1.78 .00169 .000483	608 2.23 .00118 .000352	1215 4.45 .000395 .000129

V. THE LIFETIMES OF METASTABLY BOUND MOLECULES:

It was mentioned in the introduction that the mean lifetime of metastably bound molecules will have an effect on the transport properties of gases. This is because double molecules with a lifetime less than the mean time between collisions will behave more like single molecules than double molecules. It will be seen below that except at low temperatures (the comparison is being made at a fixed density) most metastable molecules have lifetimes sufficiently long so that effects of dissociation will not have to be considered in calculations of the transport properties.

The theory of the mean lifetime of metastably bound double molecules is very similar to the one body model theory[21, 22, 23] of α-radioactivity. There are several ways of calculating mean lifetimes but we shall employ the simplest method using the W.K.B. approximation. This is the quasi-classical approach discussed in reference 22. From a classical mechanical point of view, the metastable molecule has a vibration period t. This is the time, as calculated by classical mechanics, for the system to move once back and forth across the potential well. Thus,

$$ t = 2 \int_{r_1}^{r_2} \frac{dr}{\sqrt{\frac{2}{m}(K - \phi_{eff})}} \tag{90} $$

[21] H. A. Bethe, Rev. Mod. Phys. **9**, 69 (1937). See especially part XI.

[22] E. C. Kemble, "The Fundamental Principles of Quantum Mechanics" (McGraw-Hill, 1937), Section 31.

[23] D. Bohm, "Quantum Theory" (Prentice-Hall, 1951), Ch. 12.

where r_1 and r_2 are the two turning points for a fixed value of K

and Kb^2. According to quantum mechanics, there will be a probability

of transmission, θ, that a particle hitting the potential barrier at r_2 will

penetrate the barrier. Thus, the probability of dissociation in one

second, P, is

$$P = \theta / t \qquad (91)$$

and the mean lifetime τ is

$$\tau = 1/P = t/\theta \qquad (92)$$

The transmission coefficient T can be found by the W.K.B. method

and is given by[21]

$$\theta = e^{-2G} \qquad (93)$$

where

$$G = \frac{1}{\hbar} \int_{r_1}^{r_3} \sqrt{2\mu(\phi_{eff} - K)} \, dr \qquad (94)$$

Here, r_2 is the turning point inside the potential well (see Eq. (90))

and r_3 is the turning point outside the well. For the W.K.B. method

to be applicable, G should be somewhat larger than one.

The mean lifetimes of metastably bound molecules will be calcu-

lated for systems interacting according to the Lennard-Jones (6-12)

potential. When Eqs. (78) and (7) and the reduced variables intro-

duced at the beginning of part IV are used (with $y = r^{*-2}$), Eq. (94)

becomes

$$G = \frac{\pi}{\Lambda^*} \int_{y_3}^{y_2} \sqrt{4y^6 - 4y^3 + K^* b^{*2} y - K^*} \, \frac{dy}{y^{5/2}} \qquad (95)$$

Here, Λ^* is a parameter which also appears in the quantum mechan-

ical equation of state[24] of a Lennard-Jones gas,

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[24] Reference 3, M.T.G.L., p. 421.

$$\Lambda^* = \frac{\hbar}{\sigma \sqrt{m\epsilon}} \qquad (96)$$

Also, with this change of variables, Eq. (90) for t becomes

$$t = \frac{\hbar}{2\epsilon \Lambda^*} \int_{\chi_2}^{\gamma_1} \frac{dy}{y^{1/2} \sqrt{K^* - 4y^6 + 4y^3 - K^* b^{*2} y}} \qquad (97)$$

The right hand sides of Eqs. (95) and (97) lead to hyper-elliptic integrals and hence are evaluated numerically. The details are described in Appendix B. The integrals were evaluated for several values of K^* for three different fixed values of $K^* b^{*2}$. The potential curves corresponding to these three values of $K^* b^{*2}$ are shown in Fig. 2. In Table VI, $2 \overset{*}{\Lambda} G$ and $2 \epsilon \overset{*}{\Lambda} t/\hbar$ are tabulated. Thus if the potential parameters of a gas are known, the mean lifetimes of metastably bound molecules can be estimated. Table VI also shows the mean lifetime for metastably bound argon molecules ($\overset{*}{\Lambda} = 0.186$, $\epsilon/k = 119.8^{\circ}K$). For $K^* = 0.49$, G is approximately 0.5 in the case of argon so that the W. K. B. approximation does not apply, but for the other values of K^*, G varies between 2 and 33 so that the W. K. B. approximation is valid. Since the mean time between collisions is of the order of 10^{-9} or 10^{-10} seconds at one atmosphere pressure and ordinary temperatures, one sees that most metastable argon molecules will not dissociate before undergoing a collision. The only exceptions will be molecules in metastable states which happen to have energies lying close to the top of the hump in the potential. However, at low temperatures, when the mean time between collisions increases, a larger number of metastable molecules will dissociate before a collision with another molecule. This will lead to a rather small correction in the transport coefficients of the gas.

Table VI. The Functions $2\Lambda^*G$ and $2\epsilon\Lambda^*t/h$ for Calculating the Mean Lifetimes of Metastable Double Molecules Using the Lennard-Jones (6-12) Potential

K^*b^{*2}	K^*	$2\Lambda^*G$	$2\epsilon\Lambda^*t/h$	τ_{argon} (sec.)
.64355	.02	8.18	3.75	4.75×10^7
	.04	4.74	4.28	5.25×10^{-1}
	.06	2.64	5.15	8.30×10^{-6}
	.08	1.17	6.96	3.98×10^{-9}
1.3261	.06	12.0	1.83	2.19×10^{16}
	.12	6.98	2.04	4.43×10^4
	.18	3.92	2.41	3.78×10^{-3}
	.24	1.74	3.14	3.82×10^{-8}
1.8435	.40	2.23	2.29	3.94×10^{-7}
	.43	1.49	2.56	8.52×10^{-9}
	.46	.824	3.05	2.76×10^{-10}
	.49	.199	4.53	1.42×10^{-11}

VI. THE NUMBER OF VIBRATIONAL LEVELS OF A DOUBLE MOLECULE:

During the course of this research, an equation for the maximum number of vibrational states of a dimer was obtained for the case of molecules interacting with a Lennard-Jones (6-12) potential. This equation will be derived in this section. The results obtained here will justify the use of classical mechanics instead of quantum mechanics in the evaluation of the partition functions in section III. It is known that the methods of classical statistical mechanics are applicable provided that $\Delta E \ll kT$, where ΔE is the energy difference between two neighboring quantum states of a system. In calculating ΔE for a dimer, only the change in vibrational energy need be considered because the rotational states are very close to each other except for hydrogen and helium isotopes. Thus, in the case of the Lennard-Jones potential, one must show that $\Delta E/\epsilon \ll T^*$. For example, it will be seen that for argon, there are nine vibrational levels in a potential well of depth ϵ , so that classical mechanical methods are valid if $1/9 \ll T^*$. Except for hydrogen, helium, and neon, the results below show that quantum mechanical corrections should be small for most gases at values of T^* as low as $T^* = 0.5$. For values of T^* a little larger than one, the quantum corrections for neon also become small.

According to the W.K.B. method[25], the vibrational quantum number, v, is given by the equation

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[25] L. I. Schiff, "Quantum Mechanics", (McGraw-Hill, 1955), Ch. VII.

$$\left(v + \tfrac{1}{2}\right) = \frac{2m^{1/2}}{\hbar} \int \left\{ E - \phi(r) - \frac{\hbar^2 \left(\ell + \tfrac{1}{2}\right)^2}{m r^2} \right\}^{1/2} dr \tag{98}$$

The limits of integration are the two positive zeros of the integrand, E is the energy eigenvalue, and ℓ is the angular momentum quantum number. The coefficient of r^{-2} contains[26] $\left(\ell + \tfrac{1}{2}\right)^2$ instead of $\ell(\ell + 1)$ because of the singularity in the potential at $r = 0$. Eq. (98) can be rewritten in terms of the quantum mechanical parameter Λ^*, which was introduced in Eq. (96), and the reduced quantities r^* and ϕ^*. For the Lennard-Jones potential, ϕ^* is given by Eq. (78) and

$$\left(v + \tfrac{1}{2}\right) = \frac{4}{\Lambda^*} \int \left\{ \frac{E}{4\epsilon} - \frac{1}{r^{*12}} + \frac{1}{r^{*6}} - \frac{\Lambda^{*2} \left(\ell + \tfrac{1}{2}\right)^2}{16 \pi^2 r^{*2}} \right\}^{1/2} dr^* \tag{99}$$

The integral on the right side of Eq. (99) is hyperelliptic and thus the energy eigenvalues cannot be obtained except by numerical methods. However, if we are only interested in the maximum number of vibrational states, the integrand can be simplified. First, the maximum number of vibrational states occurs when $\ell = 0$. This is because the addition of the centrifugal term makes the effective potential well narrower and less deep, and both of these factors decrease the number of energy levels. Therefore, we need only consider the case where $\ell = 0$. Under these circumstances, the coefficient of r^{*-2} is $\frac{\Lambda^{*2}}{64 \pi^2}$ which is never more than 1.50×10^{-2} (the value for He^3) and for most gases is of the order of 10^{-4}. Thus, only a small

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[26] P. M. Morse and H. Feshbach, "Methods of Theoretical Physics", (McGraw-Hill, 1953) Part II, p. 1101.

error is made by neglecting the term containing r^{*-2}. Secondly, for a bound state, E cannot be greater than zero. If E is set equal to zero in Eq. (99), the right side will in general no longer be equal to $v + \frac{1}{2}$, but the greatest integer contained in the right side of Eq. (99) minus $\frac{1}{2}$ will be the maximum value of the vibrational quantum number, v. Thus

$$v_{max} = \left[\frac{y}{\lambda} \cdot \int_1^\infty \left\{ \frac{1}{r^{*6}} - \frac{1}{r^{*10}} \right\}^{1/2} dr^* \quad - \frac{1}{2} \right] \tag{100}$$

In Eq. (100), the integration limits are the positive zeros of the integrand. In this section only, the square brackets, $\left[\quad \right]$, indicate the largest integer less than or equal to the number inclosed by the brackets.

The integral in Eq. (100) is easily evaluated in terms of the incomplete elliptic integral of the first kind[27] by making the substitution $y = r^{*-2}$. Thus,

$$v_{max} = \left[\frac{6 F(\gamma, k)}{5 \cdot 5^{1/4} \lambda} - \frac{1}{2} \right] \tag{101}$$

where

$$\gamma = \cos^{-1}\left(\frac{1}{2 + \sqrt{5}} \right) \tag{102}$$

$$k = \left(\frac{1}{2} + \frac{\sqrt{5}}{4} \right)^{1/2} \tag{103}$$

The maximum number of vibrational states, M, is equal $v_{max} + 1$ (because $v = 0$ is the first vibrational state). By inserting the numerical value of $F(\gamma, k)$ in Eq. (101), we find

$$M = \left[\frac{1.181}{\lambda} + \frac{1}{2} \right] \tag{104}$$

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[27] P. F. Byrd and M. D. Friedman, "Handbook of Elliptic Integrals for Engineers and Physicists" (Berlin: J. Springer, 1954).

Table VII shows the results for several molecules. It is interesting to note that for He^4 these calculations predict one vibrational level lying near the top of the potential well. More accurate methods show that probably no discrete levels exist. However, this result for He^4 indicates that in the case of the Lennard-Jones (6-12) potential, the W.K.B. method does give a fairly good approximation for the number of levels even when the maximum quantum number is low, while for most potentials one can only use the W.K.B. method with confidence when dealing with high quantum numbers. It should be noted that for the polyatomic molecules in Table VII, the number of vibrational levels refers to vibrations of the bound molecules and not to the vibrational levels of the individual molecules. In such cases, it is assumed that there is no coupling between the vibrations of the molecules and the vibrations within a molecule.

Table VII. The Maximum Number of Vibrational Levels for Several Dimers Using the Lennard-Jones (6-12) Potential [a]

Single Molecule	Λ^*	$\dfrac{1.684}{\Lambda^*} + \dfrac{1}{2}$	Maximum Number of Vibrational Levels in Dimer
He^4	2.67	1.13	1
Ne	.593	3.34	3
A	.186	9.54	9
Kr	.102	17.0	16
Xe	.064	26.8	26
CH_4	.239	7.54	7
N_2	.226	7.94	7
CO	.220	8.15	8
O_2	.201	8.87	8

[a] The values of the parameter Λ^* are from Reference 3, M.T.G.L., p. 423.

APPENDIX A. THE COMPUTATION OF THE COEFFICIENTS f_n OF EQ. (81) FOR THE LENNARD-JONES (6-12) POTENTIAL:

In this appendix, the numerical calculations used in finding the coefficients f_n of Eq. (81) are described. For the Lennard-Jones (6-12) potential, Eq. (58) becomes

$$M(K^*) = \int_{r_f(K^*)}^{r_h(K^*)} \left[K^* - \frac{4}{r^{*12}} + \frac{4}{r^{*6}} - \frac{K^* b_f^{*2}}{r^{*2}} \right]^{1/2} r^{*2} dr^* \tag{A-1}$$

One finds $K^* b_f^{*2}$ as a function of r_h^* by solving $d\phi_{eff}^* / dr^* = 0$ for $K^* b_f^{*2}$. Then, r_h^* is found by solving $\phi_{eff}^* (r_h^*) = K^*$. The results are

$$r_h^* = 5^{1/6} \left[1 - \frac{(4 - 5 K^*)^{1/2}}{2} \right] \tag{A-2}$$

and

$$K^* b_f^{*2} = \frac{12}{5^{5/3}} \left[1 - \frac{(4 - 5K^*)^{1/2}}{2} \right]^{2/3} \left[3 + (4 - 5K^*)^{1/2} \right] \tag{A-3}$$

Numerical methods are used to find r_f^*. The quantity, K_c^*, which is the upper limit for the integrals f_n, is needed. It is found that $K_c^* = 0.8$ by solving $d\phi_{eff}^* / dr^* = 0$ and $d^2 \phi_{eff}^* / dr^{*2} = 0$ simultaneously.

The integral, $M(K^*)$, can be written in a more convenient form for numerical integration by making the change in variables $y = r^{*-2}$. Thus,

$$M(K^*) = \frac{1}{2} \int_{y_h(K^*)}^{y_f(K^*)} \left(\frac{K^*}{y} - 4y^5 + 4y^2 - K^* b_f^{*2} \right)^{1/2} \frac{dy}{y^2} \tag{A-4}$$

and in this form it is seen that $M(K^*)$ is a hyperelliptic integral in the case of this potential. The function which is actually calculated is

$\dfrac{M(K^*)}{-\ln K^*}$; the reason for this being that as $K^* \longrightarrow 0$, $M(K^*)$ has a logarithmic infinity. To show this, we shall write $M(K^*)$ in still another form. Let $t = r^{*-3}$ in Eq. (A-1).

$$M(K^*) = \frac{2}{3} \int_{t_h}^{t_f} \left(1 - t^2 + \frac{K^*}{4t^2} - \frac{K^* b_*^{*2}}{4 t^{4/3}} \right)^{1/2} \frac{dt}{t} \qquad (A-5)$$

An upper bound for $M(K^*)$ as $K^* \longrightarrow 0$ is found by noticing that

$$\frac{t_h^4 - t_h^2}{t^2} \geq \frac{K^*}{4t^2} - \frac{K^* b_*^{*2}}{4 t^{4/3}} \qquad (A-6)$$

The equal sign holds at $t = t_h$; otherwise Eq. (A-6) is an inequality. Hence

$$M(K^*) \leq \frac{2}{3} \int_{t_h}^{t_f} \left(1 - t^2 + \frac{t_h^4 - t_h^2}{t^2} \right)^{1/2} \frac{dt}{t} \qquad (A-7)$$

From Eq. (A-2), it follows that as K^* approaches zero, t approaches $(K^*/8)^{\frac{1}{2}}$. Also, as K^* approaches zero, t_f approaches unity because $\lim r_f^*(K^*) = 1$. The right side of Eq. (A-7) is evaluated, in the limit $K^* \longrightarrow 0$ of small K^*, by letting $x = t^2$, integrating by parts (the division being $\dfrac{dx}{x^{3/2}}$ and the radical), using Eqs. (236.00) and (236.16) of Byrd and Friedman[27], and then taking the limit as $K^* \longrightarrow 0$. Thus,

$$\lim_{K^* \to 0} M(K^*) \leq -\frac{1}{3} \ln K^* - \frac{4}{3} + \frac{7}{3} \ln 2 \qquad (A-8)$$

A lower bound for $M(K^*)$ as $K^* \longrightarrow 0$ is found by noticing that for small K^*,

$$\frac{K^* b_f^{*2}}{4 t^{4/3}} - \frac{K^*}{4 t^2} \leq \frac{(K^* b_f^{*2})^{3/2}}{6 (3 K^*)^{1/2} t} \tag{A-9}$$

The equal sign holds in Eq. (A-9) for $t = \left(\frac{3 K^*}{K^* b_f^{*2}}\right)^{3/2}$; otherwise the inequality holds. (This can be verified by the usual methods of calculus.) Therefore

$$M(K^*) \geq \frac{2}{3} \int \left[-t^3 + t - \frac{(K^* b_f^{*2})^{3/2}}{6 (3 K^*)^{1/2}}\right]^{1/2} \frac{dt}{t^{3/2}} \tag{A-10}$$

In Eq. (A-10), the limits of the integral are the positive zeros of the radical. These zeros lie between t_h and t_f because t_h and t_f are the zeros of the radical in Eq. (A-5) while the integration limits of Eq. (A-10) are the zeros of a radical which is always less than or equal to the radical of Eq. (A-5) in the region of interest. When the right side of the Eq. (A-10) is integrated by parts (the division being $\frac{dt}{t^{3/2}}$ and the radical) and Eqs. (256.00), (256.11), and (256.12) of Byrd and Friedman[27] are used, we find on taking the limit as $K^* \rightarrow 0$ that

$$\lim_{K^* \rightarrow 0} M(K^*) \geq -\frac{1}{3} \ln K^* - 2 + \frac{8}{3} \ln 2 \tag{A-11}$$

Unfortunately, a better estimate of the limit, $\lim_{K^* \rightarrow 0} M(K^*)$, could not be obtained than those of Eqs. (A-8) and (A-11). Therefore, in finding the value of

$$f_n = \frac{(-1)^n}{n!} \int_0^{0.8} K^{*n} M(K^*) dK^* \tag{A-12}$$

numerically, the technique of subtracting the limiting form of $M(K^*)$ from the integrand of Eq. (A-12) and then integrating the logarithmic term analytically cannot be used. The method used consists in writing Eq. (A-12) as

$$\tau_n = \frac{(-1)^n}{n!} \int_0^{0.8} \frac{K^{*n} M(K^*)}{-\ln K^*} (-\ln K^*) \, dK^*$$

$$= \frac{(-1)^n}{n!} \int_0^{X_c} \frac{K^{*n} M(K^*)}{-\ln K^*} \, dx \qquad\qquad (A-13)$$

where

$$x = K^* - K^* \ln K^* \qquad\qquad\qquad - (A-14)$$

When $n = 0$, the integrand of Eq. (A-13) has an infinite slope at $x = 0$. However, since $\frac{M(K^*)}{-\ln K^*} = \frac{1}{3}$, and is thus finite when $x = 0$, this does not cause much error since the integrand is evaluated for closely spaced values of x. In fact, it is estimated that the error from this source in f_0 is somewhat less than 10^{-4}. For other values of n, this difficulty does not occur.

The integrand of Eq. (A-13) is evaluated at $0, \frac{X_c}{30}, \frac{2 X_c}{30}, \frac{3 X_c}{30}$, $\dots, \frac{2 X_c}{10}, \frac{3 X_c}{10}, \dots, \frac{8 X_c}{10}, \frac{25 X_c}{30}, \frac{26 X_c}{30}, \dots, \frac{29 X_c}{30}, \frac{117 X_c}{120}, \frac{118 X_c}{120}$, $\dots, x_c$. For each of these values of x, K^* was first computed and then $\frac{M(K^*)}{-\ln K^*}$ was found from Eq. (A-4). The integrand of Eq. (A-4) was computed at $y_h + n(v_f - y_h)$ for n equal to $0, \frac{1}{60}, \frac{2}{60}, \dots, \frac{2}{20}$, $\frac{3}{20}, \dots, \frac{18}{20}, \frac{55}{60}, \frac{56}{60}, \dots, 1$. Over the intervals $n = 0$ to $n = \frac{2}{20}$ and $n = \frac{18}{20}$ to $n = 1$ a seven point integration formula[28] can be used and over the intervals $n = \frac{2}{20}$ to $n = \frac{10}{20}$ and $n = \frac{10}{20}$ to $n = \frac{18}{20}$ a nine point integration formula[28] can be used. After $\frac{M(K^*)}{-\ln K^*}$ was computed, the integral of Eq. (A-13) was found by using a seven point

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[28] "Tables of Lagrangian Interpolation Coefficients", Mathematical Tables Project, Federal Works Agency, (Columbia University Press, 1948), p. XXXii.

integration formula over the intervals $\left[0, \frac{2X_c}{10}\right]$ and $\left[\frac{2X_c}{10}, \frac{8X_c}{10}\right]$,

a six point formula over the interval $\left[\frac{8X_c}{10}, \frac{29X_c}{30}\right]$, and a five point

formula over the interval $\left[\frac{29X_c}{30}, X_c\right]$. Table A-1 shows some of

the intermediate results in the calculation of f_n.

The accuracy of the numerical integrations is difficult to deter-
mine. The five figures given for f_n may not all be significant.
However, at worst, the error should not affect more than the fourth
figure in the first few f_n and the third figure in the last few f_n.

Table A.I. Some Intermediate Results in the Calculation of the Coefficients, f_n, for the Lennard-Jones (6·12) Potential.

κ	K^*	$y_h(K^*)$	$y_f(K^*)$	$K^* b_f^{*2}$	$\dfrac{M(K^*)}{-\ln K^*}$
0	0	0	1	0	.333333
.03261713	.005213260	.08674368	.9927673	.09017573	.319412
.06523436	.01203621	.1147303	.9874247	.1574795	.316324
.09785148	.01990063	.1357795	.9824368	.2201253	.313693
.1304686	.0286603	.1534773	.9775884	.2806197	.311233
.1630858	.0382080	.1691527	.9727855	.3400280	.308828
.195703	.04864304	.1834691	.9679732	.3989416	.306421
.2935544	.08460307	.2215240	.9531378	.5760716	.298868
.3914059	.1281329	.2556837	.9371599	.7582642	.290297
.4892574	.1803464	.2883739	.9193370	.9500520	.280024
.5871089	.2432392	.3212472	.8987110	1.156285	.267029
.6849604	.3202997	.3560290	.8736563	1.383790	.249439
.7828118	.4182309	.3954464	.8407798	1.644448	.222988

Table A-I. (Continued)

x	K^*	$y_h(K^*)$	$y_f(K^*)$	$K^* b_f {}^{*2}$	$\dfrac{M(K^*)}{-\ln K^*}$
.815429	.4577224	.4105130	.8268211	1.742452	.210514
.8480462	.5021311	.4271952	.8103841	1.848487	.194838
.8806633	.5531142	.4462991	.7902036	1.965242	.174151
.9132805	.6135813	.4694441	.7636372	2.097353	.144700
.9458977	.6896330	.5009508	.7232763	2.254262	.096834
.9540519	.7125942	.5115853	.7084284	2.299624	.079190
.9622062	.7379781	.5245271	.6894368	2.348636	.057611
.9703605	.7666218	.5419179	.6621725	2.402395	.030639
.9785148	.8000000	.584804	.584804	2.46237	0

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APPENDIX B.   THE COMPUTATION OF THE INTEGRALS IN

EQS. (95) AND (97):

The integral of Eq. (95) is easily evaluated by numerical inter-gration. For a given value of K^* and $K^* b^{*2}$, the integration limits y_3 and y_2 are first computed. These integration limits are the two smallest positive roots of the radical in the integrand. The integrand was computed at $y_3 + \frac{n}{6}(y_2 - y_3)$ for n equal to $0, .5, 1,$ 1.5, 2, 3, 4, 5, and 6 for all values of K^* and $K^* b^{*2}$ in Table V. For K^* equal to .02 and .04 ($K^* b^{*2}$ 0.64355) and K^* equal to .06 and 0.12 ($K^* b^{*2} = 1.3261$) the integrand was also computed for $\backslash = 0.25$ and 0.75. The integral was evaluated by using a five-point integra-tion formula[28] over the intervals $n = 0$ to $n = 2$ and $n = 2$ to $n = 6$ except when the integrand was evaluated at $n = 0.25$ and $n = 0.75$. In the latter case, a five-point integration formula[28] was used over the interval $n = 0$ to $n = 1$, a three-point formula from $n = 1$ to $n = 2$, and a five-point formula from $n = 2$ to $n = 6$.

To evaluate the integral of Eq. (97), the integration limits are computed as above. The limit y_1 is the largest positive root of the radical in the integrand. The integrand is infinite at the two end-points so near the endpoints the polynomial in the radical is approxi-mated by $(y - y_0) f(y_0)$. Here, $f(y) = (K^* - 4y^6 + 4y^3 - K^* b^{*2} y)/$ $(y - y_0)$ and y_0 indicates either y_1 or y_2. Now, $[f(y)]^{-\frac{1}{2}}$, near the endpoint y_2, or $[-f(y)]^{-\frac{1}{2}}$, near the endpoint y_1, can be expanded in a Taylor series about the endpoint. The approximation $(y - y_0) f(y_0)$ was used for the polynomial in the radical as long as the second term in the Taylor series expansion of $[f(y)]^{-\frac{1}{2}}$ or $[-f(y)]^{-\frac{1}{2}}$ was less than 1% of the constant term. When this

approximation is used, the contribution to the integral from the regions near the endpoints are easily evaluated analytically. To obtain the total value of the integral, the remaining portion between the new endpoints, y_2' and y_1', is evaluated numerically. The integrand was evaluated at $y_2' + \frac{n}{6}(y_1' - y_2')$ for n equal to 0, .5, 1, 1.5, 2, 3, 4, 4.5, 5.5, and 6. A five-point integration formula was used from $n = 0$ to $n = 2$, a three-point formula from $n = 2$ to $n = 4$, and a five-point formula from $n = 4$ to $n = 6$.
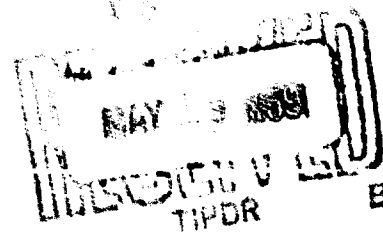
Errata for WIS-ONR-32a

1. p. 6 : Replace Fig. 2 of report by the Fig. 2 given on following pages.

2. p. 10 : Replace Fig. 4 of report by the Fig. 4 given on following pages.

3. p. 27 : Second line from bottom: $P_\phi = p_\phi /(mr^2 \sin^2\theta\, kT)^{\frac{1}{2}}$

4. p. 60 : Eq. (104) should read $M = \left[\dfrac{1.682}{\Lambda^*} + \tfrac{1}{2}\right].$

5. p. 62 : Change column heading from

$$\frac{1.684}{\Lambda^*} + \tfrac{1}{2} \quad \text{to} \quad \frac{1.682}{\Lambda^*} + \tfrac{1}{2}$$

6. p. 62 : For $\Pr$, change 17.0 to 16.99

7. p. 63 : Eq. (A-2) should read $r_h^* = 5^{1/6}\left[1 - \dfrac{(4-5K^*)^{\frac{1}{2}}}{2}\right]^{-1/6}$
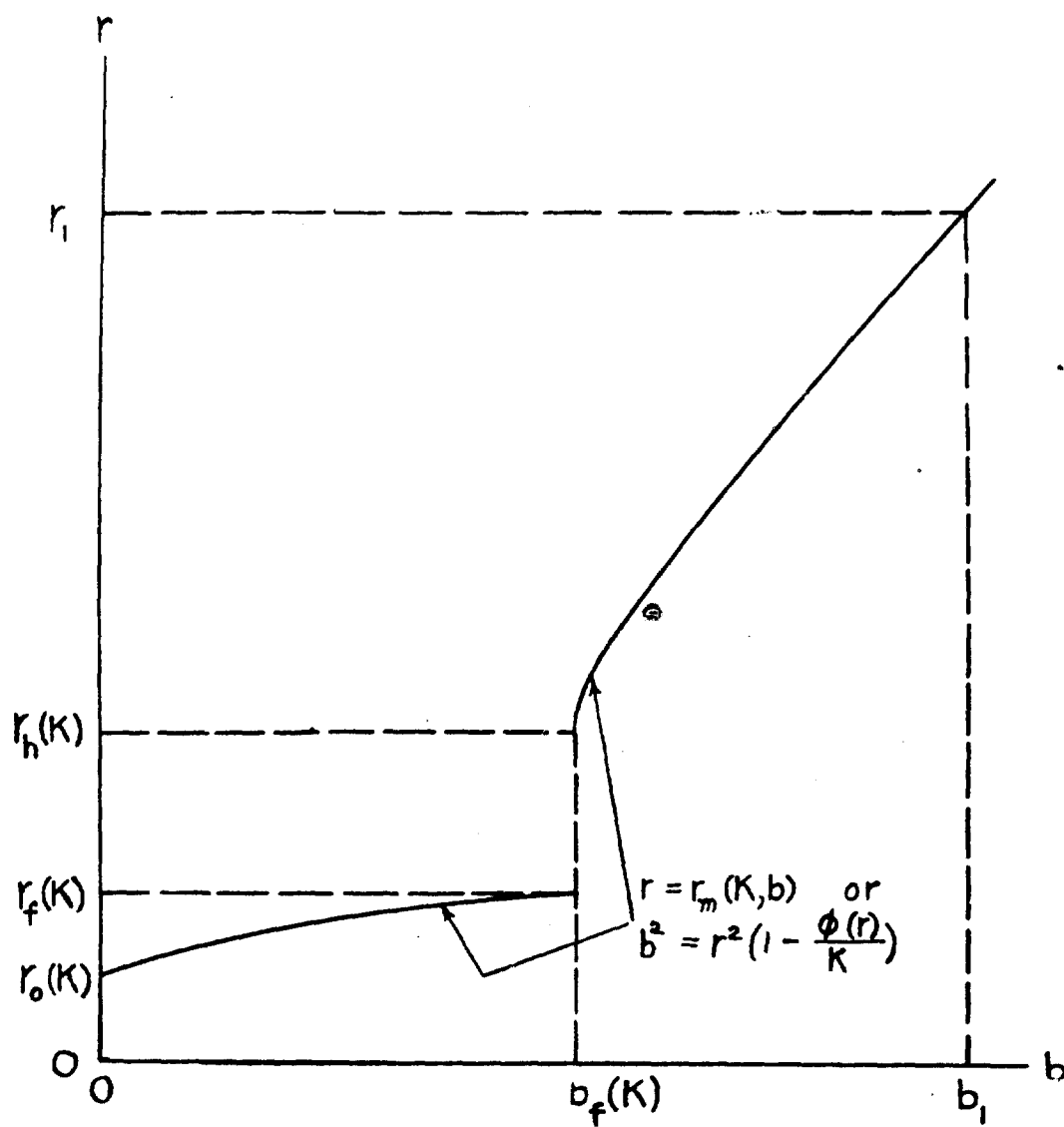
Fig. 4. The distance of closest approach r_m as a function of b for a fixed value of the initial kinetic energy K less than K_c.

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